Infrared and NMR Studies of Hydrocarbon Adsorption on Model Catalysts

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Abstract

The work described in this thesis involves the use of several techniques to investigate cyclopentene, cyclopentane and methylcyclopentane adsorption on metal surfaces. 2D NMR spectroscopy was used to study the products of the exchange reaction of methylcyclopentane with deuterium over supported metal catalysts. The distribution and extent of exchange of deuterium in the hydrocarbon was found to vary with the metal used. 2D NMR spectroscopy was used in conjunction with mass spectrometry to elucidate information on the intermediate species involved.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and transmission infrared spectroscopy were employed to follow adsorption of cyclopentene, cyclopentane and methylcyclopentane on EuroPt-1 in situ. The behaviour observed using infrared spectroscopy was correlated with behaviour in the gas phase observed using mass spectrometry and thermal conductivity in the flow system used. This allowed quantification and analysis of the reactants and products. Molecular adsorption of the three molecules was observed, and temperature programmed desorption (TPD) was used to follow behaviour with increasing temperature. This allowed the activation energy to desorption to be estimated. Cyclopentene showed complicated behaviour on heating, forming an unsaturated species on the surface. Cyclopentane and methylcyclopentane desorbed molecularly into the gas phase.

Reflection Absorption Infrared Spectroscopy (RAIRS) was used to follow adsorption and TPD of the same hydrocarbon molecules on a Pt(111) single crystal under UHV conditions. Adsorption was observed at low temperature, and multilayer build up of the three hydrocarbons was observed on increasing exposure.
I certify that unless otherwise stated all the work described in this thesis was performed by myself in the laboratories of the University of Edinburgh during the period 1990-1993.

Anne S. Dolan

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# Table of Contents

1. **Introduction**  
   1.1 Historical ................................................................................. 1  
   1.2 Adsorption and mode of action of catalysts ............................... 2  
   1.3 The form and study of catalysts ............................................. 10  
   1.4 The use of surface science in heterogeneous catalysis ............... 13  
   1.5 Multitechnique approach to surface studies ............................. 18  

2. **$^2$D NMR Study of Methylcyclopentane Exchange Reactions**  
   2.1 Introduction .............................................................................. 19  
   2.2 Exchange of hydrocarbons with deuterium ............................... 20  
   2.3 Kinetics of exchange reactions ............................................. 23  
   2.4 Application of $^2$D NMR in the study of hydrocarbon exchange reactions ........................................................................... 26  
   2.5 Experimental ........................................................................... 32  
      2.5.1 Introduction ................................................................. 32  
      2.5.2 Apparatus and Procedure ............................................. 32  
   2.6 Results .................................................................................. 37  
   2.7 Analysis of results ................................................................. 50
## 3. DRIFTS and Transmission IR study of adsorption of cyclic hydrocarbons on Pt/SiO$_2$

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Infrared Spectroscopy</td>
<td>65</td>
</tr>
<tr>
<td>3.2 The Physical Basis of Infrared Spectroscopy</td>
<td>66</td>
</tr>
<tr>
<td>3.3 Selection Rules</td>
<td>74</td>
</tr>
<tr>
<td>3.4 The application of Transmission IR and DRIFTS</td>
<td>77</td>
</tr>
<tr>
<td>3.5 The use of Transmission IR</td>
<td>79</td>
</tr>
<tr>
<td>3.5.1 Quantification of Transmission IR spectra</td>
<td>79</td>
</tr>
<tr>
<td>3.5.2 Practical Application of Transmission IR</td>
<td>81</td>
</tr>
<tr>
<td>3.6 The use of DRIFTS</td>
<td>86</td>
</tr>
<tr>
<td>3.6.1 Theory of DRIFTS</td>
<td>87</td>
</tr>
<tr>
<td>3.6.2 Experimental application of DRIFTS</td>
<td>90</td>
</tr>
<tr>
<td>3.7 The use of Fourier Transform Spectroscopy</td>
<td>92</td>
</tr>
<tr>
<td>3.8 Experimental Setup - Mass Spectrometer / TCD Flow System</td>
<td>99</td>
</tr>
<tr>
<td>3.9 DRIFTS and Transmission Spectra</td>
<td>101</td>
</tr>
<tr>
<td>3.10 Previous Work</td>
<td>105</td>
</tr>
<tr>
<td>3.11 Results</td>
<td>111</td>
</tr>
<tr>
<td>3.11.1 Cyclopentene</td>
<td>112</td>
</tr>
<tr>
<td>3.11.2 Cyclopentane</td>
<td>121</td>
</tr>
</tbody>
</table>
3.11.3 Methylcyclopentane ........................................ 123
3.12 Discussion .................................................. 124
3.12.1 Cyclopentene ............................................ 124
3.12.2 Cyclopentane ............................................ 139
3.12.3 Methylcyclopentane ..................................... 142
3.13 Summary .................................................... 147

4. RAIRS Study of Adsorption of Cyclic Hydrocarbons on Pt(111) .................................................. 184
4.1 Introduction .................................................. 184
4.2 The Physical Basis of RAIRS ................................ 185
4.3 Further Experimental Considerations ...................... 192
4.4 Comparison of RAIRS and EELS ............................ 195
4.5 Survey of RAIRS studies of hydrocarbon adsorption .... 197
4.6 Previous surface studies ..................................... 198
4.7 Experimental ................................................ 206
4.7.1 Vacuum System ........................................... 206
4.7.2 Crystal Mounting and Preparation ...................... 209
4.7.3 Infrared Setup ............................................ 216
4.7.4 Gas Handling ............................................. 218
4.8 Results ....................................................... 221
4.8.1 Cyclopentene adsorption at low temperature ........ 222
4.8.2 Blank Experiment ......................................... 225
4.8.3 Cyclopentene adsorption at ambient temperature ..... 225
4.8.4 Cyclopentane adsorption at low temperature ........ 226
4.8.5 Methylcyclopentane adsorption at low temperature 227
4.9 Discussion ........................................... 230
  4.9.1 Cyclopentene ................................. 230
  4.9.2 Cyclopentane ................................. 236
  4.9.3 Methylcyclopentane ......................... 239

5. Conclusions ........................................... 275

References ............................................ 282

A. Purity and suppliers of gases and chemicals 298

B. Properties of EuroPt-1 ........................... 299

C. Published Work ................................... 300
List of Figures

1–1 Lennard-Jones potential energy diagram. ................. 4
1–2 Potential energy profile for catalysed and uncatalysed reactions. 6
1–3 Volcano plot. ................................................. 7
1–4 Heat of adsorption as a function of coverage for some fcc metal planes. ........................................ 8
1–5 Illustration of the atomic arrangement of the (111), (110) and (100) planes of fcc and bcc metal surfaces, with the unit mesh marked. ........................................ 9

2–1 Illustration of some common intermediates observed on catalyst surfaces. ........................................ 21
2–2 Proposed rollover mechanisms for cyclopentane. ............ 22
2–3 ²D NMR spectrum from cyclopentanes. .......................... 27
2–4 Isotopic distribution of exchange reaction products. .......... 31
2–5 Schematic diagram of glass vacuum line. ......................... 33
2–6 Product distribution for experiment Pd1. ......................... 40
2–7 Product distribution for experiment Pd2. ......................... 41
2–8 Product distribution for experiment Pt1. ......................... 42
2–9 Product distribution for experiment Rh1. ......................... 43
2–10 ²D NMR spectrum of products of reaction Pd1. ............... 44
3-16 Single beam spectrum in the absence of the DRIFTS or transmission cell. .......................................................... 103
3-17 Single beam spectra recorded in (a) Transmission and (b) DRIFTS. .......................................................... 104
3-18 Normalised single beam spectra from (a) Transmission and (b) DRIFTS. .......................................................... 104
3-19 (a) Transmittance and (b) Absorbance DRIFTS spectra for cyclopentene adsorbed on EuroPt-1. .......................................................... 106
3-20 Model of cyclopentene chemistry. .......................................................... 107
3-21 EELS spectra from cyclopentene on Pt(111). .......................................................... 109
3-22 Illustration of the temporal relationship between the various techniques. .......................................................... 114
3-23 Illustration of m/z = 67 and 70 peak intensities following the fifth pulse of cyclopentene. .......................................................... 115
3-24 Plots of I vs. T and dI/dT. .......................................................... 132
3-25 Real and calculated decrease in band intensities during TPD of cyclopentene from EuroPt-1. .......................................................... 134
3-26 Illustration of cyclopentene band intensities on (a) EuroPt-1/DRIFTS, (b) Silica/DRIFTS and (c) EuroPt-1/transmission. .......................................................... 140
3-27 DRIFTS spectra of cyclopentane adsorbed on (a) EuroPt-1 and (b) silica. .......................................................... 143
3-28 DRIFTS spectra of (a) methylcyclopentane and (b) cyclopentane adsorbed on EuroPt-1. .......................................................... 145
3-29 Illustration of the differences between a DRIFTS spectrum of methylcyclopentane adsorbed on (a) EuroPt-1 and (b) silica. .......................................................... 146
3-30 DRIFTS spectra recorded during cyclopentene adsorption on EuroPt-1 at 310K. .......................................................... 150
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-31</td>
<td>DRIFTS spectra recorded during cyclopentene adsorption on EuroPt-1 at 310K (contd. from previous page)</td>
</tr>
<tr>
<td>3-32</td>
<td>Strength of absorption bands as a function of time during cyclopentene adsorption on EuroPt-1, from DRIFTS spectra in Figures 3-30 and 3-31</td>
</tr>
<tr>
<td>3-33</td>
<td>DRIFTS spectra recorded during TPD following cyclopentene adsorption on EuroPt-1</td>
</tr>
<tr>
<td>3-34</td>
<td>Expanded plots of the final two spectra during TPD of cyclopentene from EuroPt-1</td>
</tr>
<tr>
<td>3-35</td>
<td>Strength of absorption bands as a function of temperature during TPD of cyclopentene from EuroPt-1, from DRIFTS spectra in Figure 3-33</td>
</tr>
<tr>
<td>3-36</td>
<td>DRIFTS spectra recorded during H₂ pulsing at 310K following cyclopentene adsorption on EuroPt-1</td>
</tr>
<tr>
<td>3-37</td>
<td>Strength of absorption bands as a function of spectrum number during hydrogen pulsing of cyclopentene on EuroPt-1, from DRIFTS spectra in Figure 3-36</td>
</tr>
<tr>
<td>3-38</td>
<td>DRIFTS spectra recorded during H₂ pulsing following cyclopentene adsorption on EuroPt-1 and then heating to 483K</td>
</tr>
<tr>
<td>3-39</td>
<td>DRIFTS spectra recorded during cyclopentene adsorption on silica at 309K</td>
</tr>
<tr>
<td>3-40</td>
<td>Strength of absorption bands as a function of time during cyclopentene adsorption on silica, from DRIFTS spectra in Figure 3-39</td>
</tr>
<tr>
<td>3-41</td>
<td>DRIFTS spectra recorded during TPD following cyclopentene adsorption on silica</td>
</tr>
<tr>
<td>3-42</td>
<td>Strength of absorption bands as a function of temperature during TPD of cyclopentene from silica, from DRIFTS spectra in Figure 3-41</td>
</tr>
</tbody>
</table>
3-43 Transmission infrared spectra recorded during cyclopentene adsorption on EuroPt-1 at 310K. .................................................. 163
3-44 Strength of absorption bands as a function of time during cyclopentene adsorption on EuroPt-1, from transmission spectra in Figure 3-43. .................................................. 164
3-45 Transmission infrared spectra recorded during TPD following cyclopentene adsorption on EuroPt-1. .................................................. 165
3-46 Expanded plot of 463K spectrum in series of transmission TPD spectra of cyclopentene on EuroPt-1. .................................................. 166
3-47 Strength of absorption bands as a function of temperature during TPD of cyclopentene from EuroPt-1, from transmission spectra in Figure 3-45. .................................................. 167
3-48 DRIFTS spectra recorded during cyclopentane adsorption on EuroPt-1 at 309K. .................................................. 168
3-49 Strength of absorption bands as a function of time during cyclopentane adsorption on EuroPt-1, from DRIFTS spectra in Figure 3-48. .................................................. 169
3-50 DRIFTS spectra recorded during TPD following cyclopentane adsorption on EuroPt-1. .................................................. 170
3-51 Strength of absorption bands as a function of temperature during TPD of cyclopentane from EuroPt-1, from DRIFTS spectra in Figure 3-50. .................................................. 171
3-52 DRIFTS spectra recorded during cyclopentane adsorption on silica at 308K. .................................................. 172
3-53 Strength of absorption bands as a function of time during cyclopentane adsorption on silica, from DRIFTS spectra in Figure 3-52. .................................................. 173
3-54 DRIFTS spectra recorded during TPD following cyclopentane adsorption on silica. .................................................. 174
3-55 Strength of absorption bands as a function of temperature during TPD of cyclopentane from silica, from DRIFTS spectra in Figure 3-54. ................................................................. 175

3-56 DRIFTS spectra recorded during methylcyclopentane adsorption on EuroPt-1 at 309K. ................................................................. 176

3-57 Strength of absorption bands as a function of time during methylcyclopentane adsorption on EuroPt-1, from DRIFTS spectra in Figure 3-56. ................................................................. 177

3-58 DRIFTS spectra recorded during TPD following methylcyclopentane adsorption on EuroPt-1. ................................................................. 178

3-59 Strength of absorption bands as a function of temperature during TPD of methylcyclopentane from EuroPt-1, from DRIFTS spectra in Figure 3-58. ................................................................. 179

3-60 DRIFTS spectra recorded during methylcyclopentane adsorption on silica at 308K. ................................................................. 180

3-61 Strength of absorption bands as a function of time during methylcyclopentane adsorption on silica, from DRIFTS spectra in Figure 3-60. ................................................................. 181

3-62 DRIFTS spectra recorded during TPD following methylcyclopentane adsorption on silica. ................................................................. 182

3-63 Strength of absorption bands as a function of temperature during TPD of methylcyclopentane from silica, from DRIFTS spectra in Figure 3-62. ................................................................. 183

4-1 Illustration of the electric vectors of the p- and s-components of the infrared beam on a metal surface ................................................................. 186

4-2 Illustration of the parallel and perpendicular components of the p-polarised beam. ................................................................. 187
4-3 Amplitudes of electric field components relative to $E_0$ (the incident amplitude) ................................................................. 188
4-4 Illustration of variation in the surface intensity function ........ 189
4-5 Illustration of reflection from an adsorbate covered surface .... 190
4-6 Definition of the Absorption function $A$ ................................. 191
4-7 Effect on absorption spectrum for an increasing number of reflections ................................................................. 192
4-8 Illustration of the UHV system and IR Spectrometer ............. 207
4-9 Schematic illustration of the layout of the UHV system .......... 208
4-10 Illustration of the crystal mounting ....................................... 211
4-11 Schematic diagram of the operation of the LEED/Auger optics ................................................................. 213
4-12 Examples of Auger Spectra recorded for (a) a contaminated surface, and (b) a clean surface ................................. 215
4-13 RAIRS spectrum of CO adsorbed on Pt(111) ......................... 216
4-14 Illustration of the position of the crystal in the high pressure cell ................................................................. 217
4-15 Illustration of the infrared beam path from the spectrometer to the crystal ................................................................. 219
4-16 Geometry of the infrared cell and beam ................................. 220
4-17 A RAIRS single beam spectrum ................................. 222
4-18 FTIR Spectrum of cyclopentene recorded at 96K ................. 233
4-19 (a) DRIFTS spectrum of cyclopentene on EuroPt-1 and (b) RAIRS spectrum of cyclopentene on Pt(111) ......................... 235
4-20 (a) DRIFTS spectrum of cyclopentane adsorbed on EuroPt-1 and (b) RAIRS spectrum of cyclopentane on Pt(111) ......................... 238
4–21(a) DRIFTS spectrum of methylcyclopentane adsorbed on EuroPt-
1 and (b) RAIRS spectrum of methylcyclopentane on Pt(111). . 241

4–22RAIRS spectrum of Pt(111) under $1 \times 10^{-9}$ mbar cyclopentene
at 173K (3150 → 2750 cm$^{-1}$). ........................................ 243

4–23RAIRS spectrum of Pt(111) under $5 \times 10^{-9}$ mbar cyclopentene
at 173K (3150 → 2750 cm$^{-1}$). ........................................ 244

4–24RAIRS spectrum of Pt(111) under $5 \times 10^{-9}$ mbar cyclopentene
at 173K (1650 → 850 cm$^{-1}$). ........................................ 245

4–25RAIRS spectrum of Pt(111) under $5 \times 10^{-9}$ mbar cyclopentene
at 173K (3150 → $\sim$ 950 cm$^{-1}$). .................................... 246

4–26RAIRS spectrum of Pt(111) under $1 \times 10^{-8}$ mbar cyclopentene
at 173K (3150 → 2750 cm$^{-1}$). ........................................ 247

4–27RAIRS spectrum of Pt(111) under $1 \times 10^{-8}$ mbar cyclopentene
at 173K (1650 → 850 cm$^{-1}$). ........................................ 248

4–28RAIRS spectrum of Pt(111) under $1 \times 10^{-8}$ mbar cyclopentene
at 173K (3150 → $\sim$ 950 cm$^{-1}$). .................................... 249

4–29RAIRS Spectrum of cyclopentene on Pt(111) at 223K
(3150 → 2750 cm$^{-1}$). ................................................. 250

4–30RAIRS Spectrum of cyclopentene on Pt(111) at 223K
(1650 → 850 cm$^{-1}$). ................................................. 251

4–31RAIRS Spectrum of cyclopentene on Pt(111) at 273K
(3150 → 2750 cm$^{-1}$). ................................................. 252

4–32RAIRS Spectrum of cyclopentene on Pt(111) at 293K
(3150 → 2750 cm$^{-1}$). ................................................. 253

4–33RAIRS Spectrum of cyclopentene on Pt(111) at 423K
(3150 → 2750 cm$^{-1}$). ................................................. 254

4–34RAIRS Spectrum of cyclopentene on Pt(111) at 623K
(3150 → 2750 cm$^{-1}$). ................................................. 255
4–35 RAIRS Spectrum of 'clean' Pt(111) at 273K (3150 → 2750 cm\(^{-1}\)). 256
4–36 RAIRS Spectrum of 'clean' Pt(111) at 323K (3150 → 2750 cm\(^{-1}\)). 257
4–37 RAIRS Spectrum of 'clean' Pt(111) at 423K (3150 → 2750 cm\(^{-1}\)). 258
4–38 RAIRS Spectrum of 'clean' Pt(111) at 623K (3150 → 2750 cm\(^{-1}\)). 259
4–39 RAIRS Spectra during exposure of Pt(111) to (a) 5 × 10\(^{-10}\) mbar, (b) 1 × 10\(^{-9}\) mbar and (c) 1 × 10\(^{-8}\) mbar flowing cyclopentene at 303K (3150 → 2750 cm\(^{-1}\)). 260
4–40 RAIRS spectrum of Pt(111) under 5 × 10\(^{-10}\) mbar cyclopentane at 135K (3050 → 2750 cm\(^{-1}\)). 261
4–41 RAIRS spectrum of Pt(111) under 9 × 10\(^{-10}\) mbar cyclopentane at 133K (3050 → 2750 cm\(^{-1}\)). 262
4–42 RAIRS spectrum of Pt(111) under 2 × 10\(^{-9}\) mbar cyclopentane at 131K (3050 → 2750 cm\(^{-1}\)). 263
4–43 RAIRS spectrum of Pt(111) under 1 × 10\(^{-8}\) mbar cyclopentane at 128K (3050 → 2750 cm\(^{-1}\)). 264
4–44 RAIRS spectrum of Pt(111) under 1 × 10\(^{-8}\) mbar cyclopentane at 128K (1650 → 850 cm\(^{-1}\)). 265
4–45 RAIRS spectrum of Pt(111) under 1 × 10\(^{-8}\) mbar cyclopentane at 128K (3050 → ~ 900 cm\(^{-1}\)). 266
4–46 RAIRS spectrum of Pt(111) under 5 × 10\(^{-10}\) mbar methylcyclopentane at 118K (3050 → 2750 cm\(^{-1}\)). 267
4–47 RAIRS spectrum of Pt(111) under 1 × 10\(^{-9}\) mbar methylcyclopentane at 117K (3050 → 2750 cm\(^{-1}\)). 268
4–48 RAIRS spectrum of Pt(111) under 1 × 10\(^{-8}\) mbar methylcyclopentane at 117K (3050 → 2750 cm\(^{-1}\)). 269
4–49 RAIRS spectrum of Pt(111) under 1 × 10\(^{-8}\) mbar methylcyclopentane at 117K (1650 → 1250 cm\(^{-1}\)). 270
4–50RAIRS spectrum of Pt(111) under $1 \times 10^{-8}$ mbar methylcy-
clopentane at 117K (3050 → 1150 cm$^{-1}$). ............... 271

4–51RAIRS spectrum of Pt(111) under $5 \times 10^{-8}$ mbar methylcy-
clopentane at 113K (3050 → 2750 cm$^{-1}$). ............... 272

4–52RAIRS spectrum of Pt(111) under $5 \times 10^{-8}$ mbar methylcy-
clopentane at 113K (1650 → 850 cm$^{-1}$). ............... 273

4–53RAIRS spectrum of Pt(111) under $5 \times 10^{-8}$ mbar methylcyclopentan at 113K (3050 → 850 cm$^{-1}$). ............... 274
List of Tables

1–1 Some modern techniques of surface science. ................. 15

2–1 Mass Spectral and NMR analysis of cyclopentanes. ........ 28
2–2 Deuterium isotopic shifts within cyclopentane. ............. 29
2–3 Summary of experiments. ........................................... 37
2–4 Product distributions and reaction rates from mass spectral analysis. ......................................................... 39
2–5 Chemical shifts due to deuterium atoms in methylcyclopentane. 48
2–6 Isotopic shifts caused by neighbouring D atoms in methylcyclopentane. ....................................................... 49
2–7 Analysis of deuterium in exchanged methylcyclopentanes from NMR analysis for experiment Pd1. ...................... 51
2–8 NMR analysis of groupings of deuterium atoms in exchanged methylcyclopentanes. ......................................... 52
2–9 Relative exchange at each position. ............................ 55
2–10 Fractions of methylcyclopentanes exchanged in different ways. 58

3–1 Vibrations and their group frequencies. ......................... 72
3–2 Vibrations and their group frequencies contd. .................. 73
3–3 Position of IR bands observed for cyclopentene. ............ 125
3–4 Previous assignments of selected cyclopentene bands. .... 126
3–5 Position and assignment of selected bands due to cyclopentene from previous surface studies. .......................... 127

3–6 Frequencies and assignments of bands. .......................... 133

3–7 Position and assignment of bands from cyclopentane on EuroPt-1 and silica. .......................... 141

3–8 Previous assignment of selected vibrational bands due to cyclopentane. .......................... 141

3–9 Position and assignment of bands from methylcyclopentane on EuroPt-1. .......................... 144

3–10 Summary of DRIFTS vibrational frequencies determined in this study. .......................... 148

3–11 Summary of data obtained in the study of adsorption on EuroPt-1. .......................... 149

4–1 Summary of the main advantages and limitations of RAIRS and EELS. .......................... 196

4–2 Summary of EELS vibrational frequencies from previous studies. .......................... 200

4–3 Summary of vibrational frequencies of cyclopentene. .......................... 201

4–4 Vibrational frequencies and assignments of the cyclopentadienyl species, C₅H₅ (C₅). .......................... 203

4–5 Summary of literature vibrational frequencies of cyclopentane. .......................... 205

4–6 Frequencies of submonolayer and multilayer coverage of cyclopentene on Pt(111), and proposed assignment. .......................... 224

4–7 Position and proposed assignment of vibrations observed for cyclopentane on Pt(111). .......................... 227

4–8 Assignment and frequency of methylcyclopentane vibrations. .......................... 229
Chapter 1

Introduction

1.1 Historical

The first scientific definition of catalysis was made by Berzelius, writing in *The Edinburgh New Philosophical Journal*, in 1836 [1]. This statement

'Many bodies ... have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies, and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, is common in both organic and inorganic nature ... I shall ... call it catalytic power. I shall also call catalysis the decomposition of bodies by this force.'

resulted from many observations, following explosions in coal mines and observations that some metals were able to bring about reactions that otherwise did not occur. A more modern definition of the same concept is that a catalyst is a substance which increases the rate at which a chemical system approaches equilibrium, without itself being consumed in the process.

Modern theory and views of chemisorption and catalysis are still consistent with the observation made by Faraday in 1834, that adsorption of gases on solid surfaces is intimately connected with their catalytic action on
gases [2]. Some notable early observations of catalysis include the dehydrogenation of alcohol [3], the work of Haber on ammonia synthesis [4], and of Sabatier on hydrogenation [5].

Since these early beginnings, over 150 years ago, the field of heterogeneous catalysis has expanded and many studies have been undertaken, in order to attempt to understand catalysts and their mode of action. Techniques used in their study have developed from those used at that time, such as thermal conductivity and mass spectroscopy to the modern versions of photon spectroscopies and molecular beam studies of reaction dynamics.

Catalysts are used in many modern industrial chemical processes, including hydrogenation, ammonia synthesis, methanol synthesis and many others. Indeed, around 90% of all industrial processes in chemistry and petrochemistry employ catalysts [6]. One of the fastest growing applications of catalysts is their use in automotive exhaust and pollution control. Here, a platinum-rhodium catalyst is used to convert NO, CO and hydrocarbon pollutants to harmless products [7].

1.2 Adsorption and mode of action of catalysts

For a catalytic reaction to occur, the reacting species must become adsorbed on the catalyst surface. Knowledge of adsorption and the state of surfaces is necessary in order to understand catalysis. Adsorption is possible because metal atoms at the catalyst surface are not in the same environment as those in the bulk of the catalyst. Surface atoms are not coordinatively saturated and so possess a high free energy. Adsorption on the surface lowers the free energy, since the adsorbate becomes bonded to the surface. A catalyst can only alter the rate of a thermodynamically feasible reaction i.e. where \( \Delta G \), the free energy change is negative.

There are two main types of adsorption— physisorption or physical adsorption and chemisorption or chemical adsorption. In physical adsorption,
the bonds involved are similar to the van de Waals' forces involved in liquids. Typical forces involved are low, of the order of 1–5 kJmol\(^{-1}\). Physisorption is non-activated and generally occurs at low temperatures, close to the boiling point of the gaseous adsorbate, and is usually reversible. Several layers may be physisorbed to a surface. On the other hand, the forces involved in chemisorption are considerably stronger than those a molecule is subject to in a fluid, typically 20 kJmol\(^{-1}\). Chemisorption is much more specific than physical adsorption, varying from metal to metal and even between different crystal planes of the same metal. A further process, known as absorption, can occur into the bulk. Palladium is noted for dissolving hydrogen into the bulk. This is an endothermic process, distinct from adsorption.

For adsorption to occur, the free energy change, \(\Delta G\), must be negative i.e.

\[
\Delta G = \Delta H - T\Delta S
\]  \hspace{1cm} (1.1)

where \(\Delta H\) is the enthalpy change on adsorption, \(T\) is temperature and \(\Delta S\) is the change in entropy on adsorption. Usually a negative entropy change results from the constraining of a gas molecule to a 2-d surface. Consequently, \(\Delta H\) is normally negative i.e. adsorption is exothermic. Hence the extent of adsorption depends on the metal-adsorbate bond strength, and often the metal plane on which adsorption is taking place.

Adsorption can be illustrated using the classic Lennard-Jones potential energy diagram [8], Figure 1–1. In the diagram, the potential energy of the system is expressed as a function of the distance from the surface. The curve for physisorption, where the molecular adsorbate, \(A_2\), remains undisassociated, shows a shallow well representing the equilibrium state for physisorption. \(E_p\) represents the enthalpy change on physisorption. The other curve, for chemisorption of the dissociated atoms of the molecular adsorbate, \(A + A\), shows a deeper well at the position of equilibrium for chemisorption, and \(E_C\) represents the enthalpy change on chemisorption. This is at lower energy and shorter surface-adsorbate distance. Chemisorption may be an
Figure 1–1: Lennard-Jones potential energy diagram for physisorption and chemisorption, after [8].
activated process, depending on the height of the activation energy barrier, $E_a$.

The effect of a catalyst is to reduce the activation energy barrier, $E_a$, as shown in Figure 1–1, as compared with the uncatalysed reaction. This is illustrated in detail in Figure 1–2, where $E_a$ represents the activation energy required in the uncatalysed reaction and $E_b$ represents the reduced activation energy required in the presence of a catalyst. $E_d$ represents the dissociation energy required to dissociate a molecule, $A_2$, to 2A atoms.

For a catalytic reaction to proceed there must be a balance between the strength of adsorption to the surface and the catalytic activity. In the limits, weak chemisorption will lead to low surface coverage and low activity and strong chemisorption will result in a fully covered surface where the adsorbed species will be too strongly held for any reaction to proceed, resulting in poor catalytic activity. For a particular reaction, a Balandin 'volcano' plot can be drawn, relating heat of adsorption to reaction temperature for a series of metals. The heat of adsorption reflects the strength of bonding to the surface, and the reaction temperature refers to the temperature at which the metal brings about a particular rate of reaction, and is thus a measure of activity. This is illustrated for the decomposition of methanoic acid, HCOOH, to CO$_2$ and H$_2$O in Figure 1–3. Metals at or near the top of the peak with intermediate bonding strength show the highest catalytic activity and so are the best catalysts for that reaction.

Adsorption energy may also vary with surface coverage. It normally decreases as surface coverage increases, as a result of surface heterogeneity, interaction between adsorbed species or heterogeneity caused by adsorption. This is illustrated in Figure 1–4 for the three common face centered cubic (fcc) surfaces and for a stepped fcc surface. The atomic arrangement of the (111), (110) and (100) Miller index planes of an fcc and body centered cubic (bcc) metal are shown in Figure 1–5. The (111) surface has sixfold symmetry and is a 'flat' surface, whereas the (110) and (100) planes have fourfold symmetry, with the (110) surface being a particularly 'open' and
Figure 1-2: Potential energy profile for catalysed and uncatalysed reactions.
Figure 1-3: 'Volcano' plot showing the relationship between catalytic activity across a transition metal series and the heat of formation of the methanoate species from methanoic acid decomposition, adapted from [9].
Figure 1–4: Heat of adsorption as a function of coverage for some fcc metal planes.
Figure 1–5: Illustration of the atomic arrangement of the (111), (110) and (100) planes of fcc and bcc metal surfaces, with the unit mesh marked.
consequently highly reactive surface. Indeed, open/rough surfaces exposing sites of high coordination generally show especially high reactivity. Thermal Desorption Spectroscopy (TDS) studies of hydrogen adsorption on Pt(111), stepped Pt(557) and kinked Pt(12,9,8) show that stronger adsorption is seen at defect and kink sites than at flat surfaces [10]. Similarly, decomposition of ethene occurs on Ni(111), Ni(110) and stepped Ni 5(111) x (110) with bond breaking occurring at considerably lower temperature at step sites [11].

As mentioned previously, the adsorption energy may also vary with the surface e.g. the heat of adsorption may be different for each of the (111), (110) and (100) surfaces. If this leads to different reaction rates the reaction is said to be structure sensitive, whereas if catalytic reaction does not vary with surface structure, the reaction is said to be structure insensitive. An example of a structure sensitive reaction is the catalytic synthesis of ammonia over iron. The relative amounts of ammonia produced over the (111), (110) and the (100) surfaces are 418, 25 and 1 respectively [12]. A striking example of a structure insensitive reaction is for hydrogenation of benzene over several nickel surfaces. Similar turnover frequencies were found for Ni(111), Ni(110), Ni(100) and a supported nickel catalyst [13].

13 The form and study of catalysts

In general, metals are the most commonly used catalysts in catalytic reactions. No two reactions will be catalysed to the same extent by the same catalyst, and this manifests itself in the wide range and variety of catalysts in use today. Nowadays, catalysis can be divided into two forms, heterogeneous catalysis, which is of interest here, and homogeneous catalysis, usually liquid-liquid catalysis involving a liquid phase metal-ligand complex as the catalyst.

Heterogeneous catalysis usually involves a solid catalyst and gaseous reactants. The catalytic action actually involves formation and breaking
of chemical bonds between reactants and surface atoms of the solid. Since catalysis actually takes place on the solid surface, the most efficient catalysts will be those with the maximum number of surface atoms. There are various methods of preparation employed to maximise the number of metal atoms at the surface of small metal particles as opposed to large numbers of bulk atoms in the bulk of larger particles. Some examples of high surface area pure metal catalysts are Raney nickel and platinum black, both used as hydrogenation catalysts. These catalysts have surface areas of $20\text{m}^2\text{g}^{-1}$ and around $100\text{m}^2\text{g}^{-1}$ respectively.

Heterogeneous catalysts may be divided into metals and non-metals. The metals are usually those of Groups 8 - 11 i.e. the transition metals, and non-metals including metal oxides and sulphides. Metals may be pure, supported or exist as a bimetallic or alloy. The non-metals may be further divided into semiconductors, and insulators such as alumina and silica. Each type of catalyst finds a particular application.

The most commonly used form of catalysts in research and industrial processes is as a supported metal catalyst. The metal is held as small particles dispersed over the surface of a high surface area support, typically silica, alumina or carbon. Normally the support used is inert, the main function of which is to support the metal particles, which would otherwise agglomerate. However, in some cases the support, e.g. titania, is an active component of the catalyst and may be involved in a strong metal-support interaction (SMSI) [14]. Typical surface areas of supported metal catalysts are of the order of 100-300 $\text{m}^2\text{g}^{-1}$. Problems can occur with traces of the precursor metal salts and/or chemisorbed hydrogen remaining after reduction.

Evaporated metal films, wires and polycrystalline foils have been widely used in many catalytic studies. However, nowadays in addition to study of supported metal catalysts, much work is done using single crystal model catalysts. These are prepared and cleaned under ultra high vacuum conditions ($<10^{-10}$ mbar), and then adsorption and reaction are followed on a particular well defined surface, using modern techniques of surface science.
The results from such simplified systems can then be used to interpret the more complicated results of polycrystalline surfaces.

The main techniques used to follow and investigate reactions over supported metal catalysts include thermal conductivity, thermal desorption, isotopic exchange, nuclear magnetic resonance (NMR) and infrared spectroscopy (IR). The more commonly used solution state NMR technique is used to analyse reaction products collected following an experiment. The use of this technique is described further in Chapter 2. Solid state NMR has also proved useful in investigation of adsorption and catalysis [15]. NMR spectra can be recorded for NMR active nuclei in the catalyst itself or for those of adsorbates on the surface. Solid state NMR is a quasi in situ technique in that the catalyst sample must be placed within the magnetic field of the spectrometer, although it can be removed between recording spectra to alter conditions, or alternatively temperature and gas flow can be changed in situ.

The last technique mentioned above, that of infrared (IR) spectroscopy, is perhaps the most versatile and well used in the study of catalysis. IR spectroscopy has the advantage over some other techniques that it is a photon spectroscopy and is applicable in situ. An infrared source emits a wide range of frequencies, and some of these will be absorbed by metal-adsorbate vibrations when an IR beam is incident on a surface. Analysis of the outgoing radiation gives information on the metal-adsorbate bonds. These vibrate at characteristic frequencies, absorbing the appropriate frequencies of radiation, giving rise to absorption bands in the infrared spectrum. In this way, very detailed information on molecular structure and symmetry can be obtained.

Both transmission IR and Diffuse Reflectance Infrared Spectroscopy (DRIFTS) have been used to investigate adsorption in this study, and this is described in detail in Chapter 3. Study of adsorption and reaction on single crystals is described in detail in the following Section.
1.4 The use of surface science in heterogeneous catalysis

The previously described 'classical' approach to study of heterogeneous catalysis has been supplemented recently with the development of modern surface science techniques. Traditionally, high surface area supported metal catalysts have been studied, typically at pressures down to $10^{-6}$ mbar, using high vacuum glass and metal lines.

However, more sophisticated vacuum equipment has been developed, together with an array of surface techniques, for detailed investigation. The surface science approach to catalysis is to study catalytic reactions occurring in a controlled environment over a well defined single crystal surface, usually a metal. 'Surface science' developed in the early seventies, when single crystals became commercially available as a result of demand in transistor manufacture. A single crystal of a metal is grown from the ultra pure melt, and can then be cut precisely to expose one particular low Miller index plane of interest. The typical exposed area of a single crystal is $1 \text{ cm}^{-2}$, corresponding to approximately $1 \times 10^{15}$ surface metal atoms. In order to clean and characterise the crystal surface, it is held within a controlled environment, a stainless steel ultra high vacuum (UHV) chamber. UHV technology developed around the same time as single crystals became available, as a result of space research.

In the study of supported catalysts described in the previous Section, the catalyst is treated under high vacuum, with the lowest pressure achievable, around $10^{-6}$ mbar. A 'clean' surface is typically prepared by heating the catalyst under hydrogen in order to reduce the metallic component to its zero valent state, followed by outgassing under vacuum. However, no techniques are available to view the degree of cleanness of the surface at this point. In order to be able to prepare, maintain and characterise a clean single crystal surface, it is essential that the crystal is treated under UHV conditions.
This can be seen by considering the kinetic theory of gases [16]. The rate of arrival of gas phase molecules at a surface can be expressed as

\[
 r = \frac{3.51 \times 10^{22} \times P}{(TM)^{1/2}}
\]  

(1.2)

where \( r \) is in molecules cm\(^{-2}\)s\(^{-1}\), \( P \) is the pressure in Torr \(^1\), \( T \) is the absolute temperature and \( M \) is the molecular weight of the impinging gas molecules. For \( \text{N}_2 \) at 298K at 1 Torr this gives \( r = 3.84 \times 10^{20} \) molecules cm\(^{-2}\)s\(^{-1}\). The time to achieve monolayer coverage at different pressures can be calculated assuming a typical single crystal has \( 10^{15} \) adsorption sites cm\(^{-2}\). This gives times for monolayer adsorption of \( 3 \times 10^{-6} \) s at 1 Torr, 3s at \( 1 \times 10^{-6} \) Torr and 3600s at \( 1 \times 10^{-9} \) Torr. Hence in order to be able to prepare and maintain a clean surface during the course of an experiment, a vacuum of \( 10^{-10} \) Torr or better is imperative. Even at these low pressures, some surfaces, particularly the more open ones, become contaminated by residual gases in the UHV system, especially CO and hydrogen.

UHV conditions are also necessary for some of the techniques used, so that the mean free path lengths of electrons and ions in the gas phase are very long in order that they have not collided with gas phase molecules before reaching the sample.

A typical surface science type experiment involves cleaning the crystal under reactive gases or by \( \text{Ar}^+ \) bombardment. The cleanness of the surface can then be monitored using UHV techniques and surface spectroscopies. The adsorbate under study is then dosed onto the surface and adsorption and reaction are monitored.

A whole array of techniques has been developed over the past two decades. These techniques have to be particularly sensitive due to the inherently small number of adsorption sites on a typical single crystal, compared with that of typical supported metal catalysts. It is now possible to detect frac-

\(^{1}1 \text{Torr} = 1.333 \times 10^{-3} \text{ atm.}\)
tions of monolayers on single crystals under UHV conditions. Some of the most commonly applied techniques are listed in Table 1–1.

Table 1–1: Some modern techniques of surface science (with acronym).

<table>
<thead>
<tr>
<th>MASS SPECTROSCOPIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Desorption Spectroscopy (TDS)</td>
</tr>
<tr>
<td>Secondary Ion Mass Spectroscopy (SIMS)</td>
</tr>
<tr>
<td>Laser Induced Mass Analysis (LIMA)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ELECTRON SPECTROSCOPIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Energy Electron Diffraction (LEED)</td>
</tr>
<tr>
<td>Auger Electron Spectroscopy (AES)</td>
</tr>
<tr>
<td>Electron Energy Loss Spectroscopy (EELS)</td>
</tr>
<tr>
<td>High Resolution Electron Microscopy (HREM)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHOTOELECTRON SPECTROSCOPIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet Photoelectron Spectroscopy (UPS)</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHOTON SPECTROSCOPIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflection Absorption Infrared Spectroscopy (RAIRS)</td>
</tr>
<tr>
<td>Infrared Emission Spectroscopy (IES)</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
</tr>
<tr>
<td>Secondary Harmonic Generation (SHG)</td>
</tr>
<tr>
<td>Sum Frequency Generation (SFG)</td>
</tr>
<tr>
<td>X-ray Absorption Edge Fine Structure (EXAFS)</td>
</tr>
</tbody>
</table>

The techniques listed are mainly applicable to well defined single crystals under UHV conditions. Because a single crystal surface is ordered and well defined, techniques such as Low Energy Electron Diffraction (LEED) can be applied in a surface science context. In contrast, they are not applicable to supported catalysts, which have a wide range of poorly defined surfaces. Thermal Desorption Spectroscopy (TDS) may be applied in both instances, and results from the simplified single crystal study may be used to interpret more complicated thermal desorption spectra from supported metals. TDS is
a destructive technique — the adsorbate is driven off the surface and the adsorption process is analysed. In certain instances using a high beam energy, LEED can lead to desorption of a weakly held overlayer but in general it is a non-destructive technique. Reflection Absorption Infrared Spectroscopy (RAIRS) cannot be applied to supported metals, but is applicable to single crystal surfaces in the surface science context at low pressure, and using polarisation modulation at higher pressures to remove gas phase infrared absorption bands. RAIRS is only one form of infrared spectroscopy, and indeed transmission IR is one of the most widely applied of all techniques in studying catalysis. This and other relevant forms of infrared spectroscopy form the bulk of the techniques used in the study described in this Thesis.

The obvious discrepancy between experiments performed on single crystals under UHV conditions and those on supported metal catalysts is the large pressure difference between the two regimes, and this has long been recognised [17-19]. The difference is magnified further if the operating conditions of working catalysts, often hundreds of atmospheres of pressure, are considered. This has often been cited as a major disadvantage of the surface science approach to catalysis, and recently attempts have been made to 'bridge the pressure gap'. It must be borne in mind that studies of single crystals under controlled environments are studies of model systems, and in saying this, results obtained for single crystals have been used to good effect in interpreting other studies [20]. It is often possible to obtain more detailed information using model catalysts, and this can be used as reference data for real catalysts, with remarkable agreement often existing. The contribution of surface science to heterogeneous catalysis has been long debated and is well documented [19, 21-28]. Many articles on the subject of surface science have been published [10, 29-31]. New concepts, such as surface reconstruction and surface relaxation, have emerged from surface science studies.

Perhaps one of the best techniques available for the study of adsorption on single crystal model catalysts in situ is RAIRS. CO has been the most widely
studied adsorbate for several reasons, principally because it is a strong infrared absorber. More recently, it has become possible to use RAIRS to study adsorption and reaction of hydrocarbons which are more weakly absorbing [32, 33]. The first reports of RAIRS study of hydrocarbon adsorption on a single crystal surface were as recent as 1986 [34-36]. It is now possible to use RAIRS to study in situ adsorption of CO [37, 38] and of hydrocarbons [39] at high pressures. This is achieved by having a cell, capable of withstanding high gas pressures, attached to a UHV chamber, so that the crystal can be prepared and characterised under UHV conditions both before and after an experiment in which it is isolated in the high pressure cell. The advantage of in situ RAIRS used at high pressure is that weakly absorbing species with short surface residence times can be observed – they are usually pumped away as soon as the supporting gas phase is removed. Before it was possible to undertake RAIRS experiments at pressures above those which could be withstood by a UHV chamber, a number of experiments were reported on the kinetics of reactions at higher pressures [18, 40-45]. A comprehensive review of high pressure catalytic reactions over single crystal metal surfaces has been published [46]. A detailed analysis of the surface before and after reaction can now be related to the quantitative kinetics observed under realistic catalyst working conditions. The first experiment undertaken to measure the rate of a catalytic reaction at high pressure, with characterisation in a low pressure chamber, was the hydrogenation of cyclopropane on Pt(111)[47]. Turnover rates were found to be almost identical to those obtained for the same reaction over supported platinum [48, 49].

One system which exemplifies the surface science approach to heterogeneous catalysis is that of the adsorption of the simplest alkene, ethene, on both single crystal and supported metals. On Pt(111), the formation of the ethylidyne species, $\equiv$C-CH$_3$, following ethene adsorption has been detected, using a multitude of techniques. These include Temperature Programmed Desorption (TPD) [50, 51], RAIRS [32, 39, 52], EELS [53], LEED [23] and Secondary Ion Mass Spectroscopy (SIMS) [51]. There have been
several studies of ethene adsorption leading to ethylidyne formation on supported metal catalysts, including transmission IR studies on Pt/Al$_2$O$_3$ [54] and on Ni/Al$_2$O$_3$ [55], and DRIFTS on Pt/SiO$_2$ and Ni/Al$_2$O$_3$ [56]. Using infrared spectroscopy \textit{in situ}, the concentration of ethylidyne on the surface can be determined by following the intensity of the $\delta_{sy}(\text{CH}_3)$ band at $\sim 1335$-1340 cm$^{-1}$. Solid state NMR has also been used to investigate ethylidyne formation kinetics, in the form of $^2$H NMR Spectroscopy [57]. The application of the surface science type study is vindicated by a comparison of the single crystal and supported catalyst results, showing that the adsorbed species vary with both the metal substrate and the crystal plane involved.

1.5 \textbf{Multitechnique approach to surface studies}

The approach to the study of catalytic reactions described in this Thesis involves the use of several techniques. Firstly, deuterium exchange experiments are described, involving the exchange of methylcyclopentane with deuterium over several silica supported metal catalysts. These reactions were followed using mass spectroscopy and the reaction products were collected and analysed using $^2$D NMR spectroscopy.

The remainder of this Thesis is concerned with the application of infrared spectroscopy to observe vibrations of species adsorbed on surfaces. In Chapter 3, Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) and transmission infrared spectroscopy are used to investigate the adsorption and temperature programmed desorption of cyclopentene, cyclopentane and methylcyclopentane on EuroPt-1, a well characterised Pt/SiO$_2$ catalyst. The same cyclic hydrocarbon molecules were then investigated using Reflection Absorption Infrared Spectroscopy (RAIRS) on a Pt(111) single crystal model catalyst.
Chapter 2

$^2$D NMR Study of Methylcyclopentane Exchange Reactions

2.1 Introduction

A powerful way of determining information on mechanisms which take place on a catalyst surface is the use of isotopic exchange reactions. Catalytic exchange of hydrocarbons with deuterium has been widely investigated over several decades. Although reaction intermediates are not observed directly, the end products of an exchange reaction reveal information on the nature of possible adsorbed hydrocarbon intermediates from the number and position of deuterium atoms incorporated into the molecule prior to desorption into the gas phase. Essentially, this technique uses the deuterium isotope as a label, which is incorporated into short lived intermediates, and analysis of the end products can be used to extrapolate back to determine the reactivity and relative importance of various possible intermediates.
2.2 Exchange of hydrocarbons with deuterium

The history of exchange reactions with deuterium can be traced back to 1946, when the deuterium isotope first became available for catalytic studies [58]. Initially, exchange reactions with deuterium were followed, using techniques such as microwave spectroscopy, for example to study propene-D$_2$ exchange [59], infrared spectroscopy [60], thermal conductivity measurements of the dilution of deuterium by hydrogen [61] in the exchange of deuterium with n-hexane and cyclohexane, and even combustion analysis, to determine the deuterium content of the hydrocarbon under study [62].

Subsequently, with developments in mass spectrometer instrumentation, a vast field of catalytic exchange reactions opened up. Many papers were published, the earliest examples being methane exchange with deuterium over a Fischer-Tropsch cobalt catalyst [63] and over evaporated nickel films [64], as well as studies of the exchange between CH$_4$ and CD$_4$ [65-67] and the exchange of hydrocarbons with deuterium on palladium catalysts [68].

Since these early studies, many investigations have been carried out, and the whole subject of exchange reactions has been reviewed [69, 70]. Exchange of higher alkanes with deuterium over supported metal catalysts and evaporated metal films has been studied extensively [71]. Some rather unusual molecules have been used to test particular exchange mechanisms. Bicyclo[2,2,1]heptane [68], norborane [68] and adamantane [72] show very limited exchange distributions, due to molecular geometry preventing propagation of exchange around the molecule.

The exchange reactions of cyclic hydrocarbons have been investigated. Cyclopentane has been one of the most highly studied molecules, over several different metals [73-75] and is discussed below to illustrate some of the processes undergone by the molecule. Unlike linear alkanes, rotation is restricted about the carbon–carbon bonds of a cyclic molecule. Formation of D$_1$ to D$_5$ cyclopentanes can be explained by a mechanism involving
interchange between $\alpha$ and $\alpha\beta$ diadsorbed cyclopentane, known as the $\alpha\beta$ mechanism [76, 77]. Some of the most common intermediates are illustrated, with their commonly used nomenclature, in Figure 2-1.

![Illustration of some common intermediates observed on catalyst surfaces.](image)

Molecules containing more than five deuterium atoms must either be formed from more than one visit to the catalyst surface or by some mechanism which can propagate exchange to the other side of the ring. Experiments at low temperatures over platinum, rhodium and nickel showed considerable $D_5$ formation and a small extent of exchange beyond this [73], as well as a variation in the distribution with the metal. However, over a Pd/Al$_2$O$_3$ catalyst at 313K, a substantial amount of $D_{10}$ and some $D_8$ was formed, in addition to a maximum at $D_5$ [68, 78], with the size of the maximum at $D_{10}$ increasing with temperature. Similar behaviour was also observed for an evaporated platinum film at 273K [73]. It was reported that at least five distinguishable processes with varying activation energies were thought to be involved in the exchange of cyclopentane with deuterium over palladium [78]. The mechanism for the turnover of the cyclopentane ring is thought to be a rollover mechanism, as illustrated in Figure 2-2. The
hydrogen atoms on each side of the ring are illustrated as H or h to clarify each side of the ring.

Figure 2-2: Proposed rollover mechanisms for cyclopentane.

In this mechanism, the $\alpha\beta$ diadsorbed cyclopentane rolls over on the catalyst surface through a vertically adsorbed alkene species, thus transferring adsorption to the other side of the ring and enabling the hydrogen atoms there to be exchanged. This mechanism can explain the minor peak at $D_8$, if $D_3$ cyclopentane rolls over and exchanges the five hydrogen atoms on the other side of the ring, as well as the maximum at $D_{10}$, if there is easy multiple rollover.
2.3 Kinetics of exchange reactions

When an isotopic exchange reaction is being followed using mass spectrometry, a small sample of the reaction mixture is taken at regular intervals or drawn off continuously to be analysed. From analysis of the set of mass spectra recorded, much information can be gained on the kinetics of the reactions occurring on the surface of the catalyst, and hence on the predominant mechanisms. Any such mass spectrum obtained consists of a set of peaks of intensity proportional to the amount of each isotopic species present. Usually the assumption is made that the probability of ionisation of a species in the mass spectrometer is independent of the number of hydrogen or deuterium atoms in the molecule [62]. This assumption has been justified [79].

The mass spectra recorded must be corrected for naturally occurring $^{13}$C (1.1%) and $^2$D (0.02%). Consideration must also be given to formation of fragment ions from one isotopic species having the same mass/charge ratio as peaks from other species. This problem can be reduced by using as low an ionising voltage as possible to minimise fragmentation but still achieve reasonable sensitivity.

The detailed analysis of exchange reactions described by Kemball [62] is summarised below. The course of an exchange reaction is followed by the mean deuterium content of the hydrocarbon molecule under study, $\Phi$, or a parameter related to this. If $\Phi$ is defined as

$$\Phi_t = d_1 + 2d_2 + 3d_3 + \ldots nd_n$$

(2.1)

where $d_i$ is the percentage of the total hydrocarbon $^1$ present as the isotopic species containing $i$ deuterium atoms i.e. $C_xH_{n-i}D_i$ at time $t$.

---

$^1$Hydrocarbon is used here to represent all isotopic species
The course of the exchange reaction can be described by the rate equation

$$\frac{d\Phi}{dt} = k_\Phi \left( 1 - \frac{\Phi_t}{\Phi_\infty} \right) \quad (2.2)$$

where $k_\Phi$ is a rate constant for the number of deuterium atoms entering 100 hydrocarbon molecules in unit time, during the early stages of the reaction, and $\Phi_\infty$ is the equilibrium value of $\Phi$. $\Phi_\infty$ can be estimated, assuming that in the equilibrium distribution the hydrogen and deuterium atoms are randomly distributed in the hydrocarbon and 'hydrogen' mixture. $\Phi_\infty = x_D \times n \times 100$, where $x_D$ is the fraction of deuterium atoms in the total number of hydrogen and deuterium atoms in the system and $n$ is the number of exchangeable hydrogen atoms in the hydrocarbon.

Integration of this equation gives

$$-\log_{10} (\Phi_\infty - \Phi_t) = \frac{k_\Phi t}{2.303\Phi_\infty} - \log_{10} (\Phi_\infty - \Phi_0) \quad (2.3)$$

where $\Phi_0$ is the initial value of $\Phi$.

Although the assumption that all isotopic species react at the same rate was used in the above argument making the equations only approximately true, the equations were found to hold for many exchange reactions [62].

From the integrated equation, it can be seen that for a first order reaction a plot of $\log_{10} (\Phi_\infty - \Phi_t)$ vs. $t$ will give a straight line with gradient $-k_\Phi/2.303\Phi_\infty$. Hence for a first order reaction, the rate constant $k_\Phi$ can be determined. If the equation holds, it is implicit that all hydrogen atoms in the hydrocarbon are equally exchangeable.

Sometimes the first order rate equation does not hold - the assumption that all isotopic species are equally likely to fragment may not be valid. This is discussed further in Section 2.5.2. Another problem can be poisoning of the catalyst during the course of reaction.

Another way of following an exchange reaction is to determine the rate constant, $k$, representing the rate of disappearance of the light hydrocarbon (i.e. that containing only hydrogen atoms). For $k$ expressed as a percentage
per unit time, then

\[ -\log_{10}(D_0 - D) = \frac{kt}{2.303(100 - D_\infty)} - \log_{10}(100 - D_\infty) \]  

(2.4)

where \( D_0 \) is the percentage of light hydrocarbon at time \( t \) and 100 and \( D_\infty \) are the initial and final percentages of the light hydrocarbon.

The rate constant \( k \) can be determined by plotting a graph of \( \log(D_0 - D) \) vs. \( t \). This graph will again give a straight line for a first order reaction, and the ratio of the two rate constants, known as the multiplicity, defined as

\[ M = \frac{k_\Phi}{k} \]  

(2.5)

represents the mean number of hydrogen atoms replaced by deuterium atoms in each hydrocarbon molecule undergoing exchange in the initial stages of reaction. A value of \( M \) close to unity indicates that one hydrogen atom is replaced by one deuterium atom on one visit to the surface, i.e. exchange is stepwise. When \( M \) is greater than one, multiple exchange occurs, with several hydrogen atoms being exchanged on one visit to the surface. In a multiple exchange reaction there will be immediate appearance of highly deuterated product molecules in the initial product distribution.

It is important to bear in mind that the rate equations – and hence the rate constants just described – refer to initial stages of reaction when the hydrocarbon has visited the surface once. At some point the equations may no longer hold, due to poisoning of the catalyst or to dilution of the deuterium, as discussed in the previous Section. This is reflected by a curvature in the plots. However, the initial gradient can be used to obtain the rate constants \( k \) and \( k_\Phi \). These initial rates and product distributions are of interest to establish the mechanisms involved in the exchange into the hydrocarbon from only one visit to the catalyst surface.

The chance of a molecule visiting the catalyst surface more than once can be calculated using the addition law of probability. This states that when there are several possible ways for an event to occur, the probability of an event occurring in one way is the sum of the probabilities of the occurrence
in each of the different possible ways [80]. Hence, when one molecule out
of one hundred has reacted on the surface, the chance of the same molecule
visiting the surface again is \( \frac{1}{99} \). Thus at 15\% reaction, \( \frac{1}{99} + \frac{2}{98} + \frac{3}{97} + \ldots + \frac{15}{85} = 1.24\% \) will have reacted twice, and at 20\% reaction this proportion increases
to 2.34\%.

The values of \( k_0 \) and \( k \) are specific to the one experiment. They will be
affected by reactant pressures. A full study of reaction kinetics requires
several experiments using varying initial pressures, since only one plot of
\( \log_{10}(\Phi_\infty - \Phi) \) vs. \( t \) may not reflect the true kinetics of the reaction.

### 2.4 Application of \(^2\!D\) NMR in the study of hydrocarbon exchange reactions

More recently, with high field NMR instruments being developed and becom-
ing more readily available in the 1970s, along with computer line narrowing
techniques, the study of exchange reactions of hydrocarbons with deuterium
has been further developed. A high field spectrometer is required since the
isotopic shifts are of the same order as the width of the resonances. The
deuterium isotope, \(^2\!D\), is an NMR active nucleus with spin = 1, and despite
its very weak signal, it can now be routinely studied on modern high field
Fourier Transform (FT) spectrometers.

The major advantage of the use of \(^2\!D\) NMR spectroscopy in studying ex-
change reactions is that the position of the deuterium atoms incorporated
into the hydrocarbon molecule can be unambiguously determined. The po-
tential of this technique was first realised with a study of catalytic reactions
of cyclopentene over zinc oxide [81]. The exchange of deuterium into cy-
clopentene occurs, as well as the addition reaction to form cyclopentanes
which occurs at a slower rate.
The $^2$D NMR spectrum for the isotopic cyclopentenes produced in the exchange reaction showed resonances at $\delta = 5.78$ and 2.31 ppm due to D being exchanged at the alkene carbon atoms and the adjacent allylic carbon atoms respectively. Integration of the area under these peaks showed that most deuterium was incorporated at the alkene carbon atoms. The $^2$D NMR spectrum recorded for the isotopic cyclopentanes produced from addition of deuterium to cyclopentene over zinc oxide provided more information, and is shown in Figure 2–3. The $^2$D NMR spectra from the isotopic cyclopentanes were analysed and results compared with mass spectral data, and showed the potential use of $^2$D NMR spectroscopy in identification and quantification of deuterium in products of such reactions. These spectra show resonances at $\delta = 1.501, 1.494, 1.482, 1.476$ and 1.468 ppm. The position of a resonance in an NMR spectrum depends on the location of the atom in the hydrocarbon molecule and also on any additional isotopic shifts caused by neighbouring deuterium atoms in the same molecule. The chemical shift, $\delta$, is normally of the order of parts per million (ppm) and the isotopic shifts are smaller, shifting the resonance several parts per billion (ppb) downfield.

The resonances listed above were thought to be due to D$_1$-cyclopentane at $\delta = 1.501$, 1,2-D$_2$-cyclopentane at $\delta = 1.494$, 1,1,2-D$_3$-cyclopentane at both
The NMR spectra could also be used quantitatively to determine the relative quantities of each species produced. The data from integration of the areas under the NMR resonances is shown in Table 2-1. These show good agreement with calculations made from mass spectral analysis of the reaction. Hence, it was observed that the isotopically substituted cyclopentanes could be identified using $^2$D NMR, and the relative quantities of each determined.

Following on from the study of cyclopentene reactions over zinc oxide, a series of (deuterium) isotopically substituted cyclopentanes was prepared in order to accurately determine the isotopic shifts caused by neighbouring deuterium atoms in the molecule [82]. This was done on the basis of the chemical shift of the analogous H containing compound, and then with consideration of the additional isotopic shift. The shifts determined are listed in Table 2-2. Hence, with a knowledge of these shifts, the distribution of deuterium atoms in isotopically substituted cyclopentane molecules can be
Table 2–2: Deuterium isotopic shifts within cyclopentane.

<table>
<thead>
<tr>
<th>Shift</th>
<th>-Δδ / ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>17.9</td>
</tr>
<tr>
<td>β&lt;sub&gt;cis&lt;/sub&gt;</td>
<td>7.0</td>
</tr>
<tr>
<td>β&lt;sub&gt;trans&lt;/sub&gt;</td>
<td>8.3</td>
</tr>
<tr>
<td>γ&lt;sub&gt;cis&lt;/sub&gt;</td>
<td>1.9</td>
</tr>
<tr>
<td>γ&lt;sub&gt;trans&lt;/sub&gt;</td>
<td>0.3</td>
</tr>
</tbody>
</table>

established and groupings of deuterium atoms can be identified from the position of the resonances.

Further study has been made of cyclopentane exchange using 2D NMR spectroscopy [83], and of the exchange of some alkanes over silica supported platinum and rhodium catalysts [84-86]. More unusual molecules, including diethylether and tetrahydrofuran, have shown the use of 2D NMR in investigating exchange accompanied by hydrogenolysis, as well as the apparent blocking effect of the ring oxygen atom [87], and exchange of ketones with deuterium [88].

Following the successful 2D NMR study of the exchange reaction of cyclopentane with deuterium, methylcyclopentane was selected as an interesting test molecule to investigate using 2D NMR spectroscopy, and to investigate the propagation of exchange from the ring hydrogen atoms into the methyl group. Unlike cyclopentane, which has two equivalent sets of hydrogen atoms, methylcyclopentane has two inequivalent sets of ring hydrogen atoms, as well as the set of methyl hydrogen atoms. The methyl group acts as an additional 'handle' to investigate the extent of exchange beyond ring hydrogen atoms. Preliminary experiments showed that methylcyclopentane was suitable for study using 2D NMR spectroscopy, since deuterium atoms in different locations in methylcyclopentane were found to have different chemical shifts. Generally the use of 2D NMR spectroscopy is limited to molecules with restricted conformation so that individual resonances can be distinguished. The resonances were found to be further split by isotopic
shifts resulting from neighbouring deuterium atoms in the same molecule. The investigation of methylcyclopentane exchange with deuterium over several metals, using the combined techniques of mass spectrometry and 2D NMR spectroscopy, is described in Section 2.5.

The exchange reaction of methylcyclopentane with deuterium over Pd-alumina was investigated using mass spectrometry as long ago as 1957 [68, 76, 78]. The distribution of isotopic products obtained from one of these experiments is reproduced in Figure 2-4. There are clear discontinuities in the distribution after D₄, D₈ and at D₁₂ methylcyclopentanes. This can be explained by considering the hydrogen/deuterium atoms in the molecule. The twelve 'hydrogen' atoms can be grouped into three sets; the three in the methyl group, the four on the side of the ring cis to the methyl group, and the remaining five on the other side of the ring. Exchange can propagate within or between these groups by invoking various intermediates and mechanisms. The set of four hydrogen atoms on the side of the ring cis to the methyl group can exchange via interconversion between mono- and di-adsorbed alkane species, which may explain the break at the D₄ product. If adsorption onto the surface is initially via the other side of the molecule, then the group of five hydrogen atoms can exchange in a similar manner, and this may also propagate into the methyl group via an eclipsed 1,2-diadsorbed species. This would give rise to a maximum in the distribution at D₈. There must also be some mechanism operating to enable exchange to propagate between both sides of the molecule in order to get the products up to D₁₂.

With no further experimental evidence available at that time, it was concluded that the experimental distribution was made up of a sum of contributions from molecules initially adsorbed on each side, and thus leading to different relative quantities of each possible product. Now, with the use of 2D NMR spectroscopy, previously established mechanisms have been further investigated. This is discussed in Section 2.9.
Figure 2-4: Isotopic distribution of products from exchange of methylcyclopentane with deuterium over Pd-alumina at 313K, from [76].
2.5 Experimental

2.5.1 Introduction

The experiments described in this Chapter involve the exchange of methylcyclopentane with deuterium over several silica supported metal catalysts. The course of each reaction was followed by mass spectrometry and at the end of each reaction, the hydrocarbon was collected and analysed using 2D NMR spectroscopy. Details of the experiments and subsequent analysis are presented in Sections 2.5.2 and 2.7. Details of purity and suppliers of all chemicals and gases used are listed in Appendix A.

2.5.2 Apparatus and Procedure

All experiments were carried out using a mercury diffusion pumped recirculating glass line. This is illustrated schematically in Figure 2–5. The vacuum line consists of two separately pumped regions. The gas handling section was pumped separately from the remainder of the line which included the reaction vessel and the recirculating loop. Each section is pumped by one three-stage diffusion pump backed by an Edwards ED50 oil rotary pump. Liquid nitrogen traps were used between the diffusion pumps and the vacuum line to minimise contamination by mercury. All taps on the line were Springhams high vacuum ground glass stopcocks, and were lubricated with Apiezon L high vacuum grease. The vacuum was monitored using a McLeod gauge, and was typically $1 \times 10^{-6}$ mbar.

The catalysts used in this study were all $10^{-4}$ mole g$^{-1}$ of metal on a silica support, as described previously [85, 89, 90]. The preweighed catalyst was placed in a detachable reaction vessel, held loosely between two glass wool plugs. The reaction vessel was attached to the recirculating loop via two ground glass spherical joints lubricated with Apiezon T grease. These
Figure 2-5: Schematic diagram of glass vacuum line.
joints were then firmly held by lockable spring clips. The temperature of the catalyst was constantly monitored via a type K chromel-alumel thermocouple situated in a small well on the outside of the reaction vessel, adjacent to where the catalyst was situated. The reaction vessel was heated using a close-fitting electrical furnace, controlled by a Eurotherm proportional temperature controller. This maintained the catalyst at the desired temperature, using feedback of the catalyst temperature from the thermocouple to adjust the furnace output accordingly.

The hydrogen for catalyst reduction was passed through an Englehard Deoxo unit to remove any oxygen present, and then over a zeolite 4A molecular sieve to remove any water. Hydrogen was then admitted to the line, and when the hydrogen pressure in the line was one atmosphere an outflow tap was opened to set up a continual flow of hydrogen over the catalyst. During reduction the hydrogen flowed through the vacuum line at a rate of 3ml s\(^{-1}\), monitored using a floating head rotameter in the recirculating loop. The catalyst was then reduced under flowing hydrogen at 673K for one hour. The hydrogen flow was then stopped and any remaining hydrogen was evacuated from the line. The catalyst temperature was then increased by 50K and the catalyst was heated under vacuum for 30 minutes prior to cooling to the reaction temperature.

Deuterium was stored in a bulb on the gas handling section. Prior to use, it was purified by passing through a heated palladium-silver alloy thimble, and then through a liquid nitrogen cooled trap to a previously evacuated bulb. Methylcyclopentane, a liquid at room temperature and pressure, was stored in an evacuated glass vessel sealed with a teflon ‘Rotaflo’ tap, and could be attached to the gas handling line as required via a ground glass joint. Before use, the methylcyclopentane was purified by two or three freeze/thaw cycles.

The reactants were mixed and equilibrated in the gas handling section prior to admission to the catalyst. Firstly, after purification as described above, the desired amount of methylcyclopentane, as measured using a mer-
cury manometer, was expanded into the mixing volume where it was degassed in another freeze/thaw cycle. It was then frozen down again, during expansion of deuterium from the storage bulb on the glass handling line into the same volume. The cold trap was then removed and the two gases allowed to equilibrate for \( \sim 20 \) minutes. After equilibration, the reactants were expanded into the recirculating loop, but bypassing the isolated catalyst. The gases were pumped round this volume using a Metal-Bellows Corporation (MB21E) all metal reciprocating pump. The flow rate used was \( \sim 30 \text{ ml s}^{-1} \), as measured using the rotameter, to ensure that reaction rates were not limited by pumping speed. Typically, a pressure of 0.029 bar of methylcyclopentane was used in a volume of 360 cm\(^3\), giving a charge of \( \sim 2.5 \times 10^{20} \) hydrocarbon molecules. Deuterium was used in a five-fold excess in order to minimise isotopic dilution by hydrogen during the exchange reaction.

When the catalyst was at the reaction temperature, the reactants were admitted to the catalyst, and the exchange reaction began. The reaction was then followed by recording mass spectra at suitable intervals, until it had progressed to between 15 and 20\% exchange, \textit{i.e.} 85-80 \% of the starting quantity of methylcyclopentane was still unreacted, the optimum amount for subsequent \( ^2 \text{D} \) NMR analysis. A capillary leak from the recirculating loop was connected to a VG Micromass 601 mass spectrometer. This is a fast scanning 90\(^\circ\) magnetic sector instrument. The quantity of reaction mixture drawn off was very small, of the order of 2\% hour\(^{-1}\). In the mass spectrometer, the molecules were ionised using 25eV electrons produced by a tungsten filament. The ionising voltage was selected as a compromise between minimum fragmentation and maximum sensitivity. Using 25eV electrons, the parent ion of methylcyclopentane (m/z = 84) was monitored, and minor peaks were observed at m/z = 83 (5\% relative to m/z = 84 peak) and 82 (1\% relative to m/z = 84 peak).

The region around the parent ion, including fragments and deuterated species, was scanned by increasing the magnetic field strength while maintaining a constant accelerating voltage. The spectra produced were recorded
on a fast response potentiometric Kipp and Zonen BD40 chart recorder. The peaks were amplified to maximise their height on the recorded spectra. The peak heights were then measured and subsequently analysed using a computer program, making several corrections to the recorded intensities [91, 92]. The program was used to correct the experimentally recorded spectra for the contribution from naturally occurring isotopes, and for fragmentation due to loss of hydrogen or deuterium, and was used to calculate the actual percentage of each isotopic species present. The program also takes into account that due to the kinetic isotope effect, C—D bonds are less likely to break than C—H bonds and hence there is a greater chance of loss of hydrogen than deuterium during fragmentation of a molecule containing both in the mass spectrometer. Also, the dependence of the chance of fragmentation of C—H and C—D bonds on the nature of other bonds in the molecule was included. A further correction was made for the contribution of fragmented high mass species to peaks due to less exchanged molecules. The reliability of these corrections was assessed by comparing the fragment peak intensities in the corrected peak intensities with those in the recorded spectra. Typically, a 15 mass unit scan took 4 minutes to record.

The reaction was stopped by isolating the catalyst, and a final mass spectrum was recorded before the hydrocarbon was frozen down into a cold finger on the gas handling section. The collection of hydrocarbon was monitored by following the decay of the peak due to the parent ion using the mass spectrometer. The deuterium was then evacuated and the hydrocarbon was distilled into a 5mm NMR tube containing 0.5cm³ of 5% CDCl₃. The tube was then flamed to form a permanent seal, and the sample was subsequently analysed using ²D NMR spectroscopy.

The ²D NMR spectra were recorded using a Brüker WH360 spectrometer operating at 55.28 MHz and using the Aspect 3000 data system. This resonance frequency for deuterium corresponds to 360 MHz for proton resonance, the magnetic field strength being 8.46 Tesla. The deuterium in the 5% CDCl₃ solvent used to collect the sample acted as an internal reference taken as δ =
7.25 ppm. Spectra were recorded at 298K and broad band proton decoupling (1.25W) was used. A satisfactory signal to noise ratio was obtained from approximately 200 transients using a 70° pulse, spectral width of 500 Hz and 8000 data points. This gave an acquisition time of 8.2 seconds. The data was expanded to 64 000 data points before Fourier Transformation of the accumulated signal, giving a digital resolution of 0.006ppm (0.016 Hz) per data point. The resonance positions were determined accurately using line narrowed spectra, since they could not be determined accurately using the directly transformed spectra. This is because the small isotopic shifts are of a similar magnitude to the line widths of resonances. Line narrowed spectra were obtained by multiplication of the accumulated decay signal by a double exponential function before expansion of the dataset. This involved careful selection of the function parameters GB and LB in the Brüker NMR program FTQ 82061 to optimise resolution without the introduction of spurious features. All spectra presented in this Chapter have been line narrowed.

2.6 Results

Details of the experiments carried out are summarised in Table 2–3. One

<table>
<thead>
<tr>
<th>Expt</th>
<th>Catalyst weight/ mg</th>
<th>T / K</th>
<th>Extent of exchange / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd1</td>
<td>197.6</td>
<td>293</td>
<td>14.9</td>
</tr>
<tr>
<td>Pd2</td>
<td>101.1</td>
<td>333</td>
<td>19.3</td>
</tr>
<tr>
<td>Pt1</td>
<td>31.4</td>
<td>333</td>
<td>17.5</td>
</tr>
<tr>
<td>Rh1</td>
<td>48.8</td>
<td>333</td>
<td>17.3</td>
</tr>
</tbody>
</table>

experiment at 333K using each metal, and an additional reaction over palladium at 293K were carried out. The final column in Table 2–3 shows the extent of exchange, as determined using mass spectrometry when the reac-
tion was stopped. This final product distribution is of interest in order to correlate the mass spectrometric and NMR results. Initial reaction rates were investigated but no detailed analysis of the initial product distributions was necessary in this study. The initial rate of reaction is also listed in Table 2–4.

In all the experiments, the full range of possible deuteromethylcyclopentanes was formed. The relative amounts of each are shown in Table 2–4. The product distributions determined using mass spectroscopy are also shown graphically in Figures 2–6, 2–7, 2–8 and 2–9.

The final line in Table 2–4, $M_z$, shows the average deuterium content of each product molecule. At this stage, the assumptions that can be made are that $D_1$–$D_5$ products represent molecules exchanged on one side of the ring only, that $D_6$–$D_8$ are probably molecules exchanged on the open side and also in the methyl group, and $D_9$–$D_{12}$ are molecules exchanged on both sides and in the methyl group.

The $^2$D NMR spectra, recorded for the hydrocarbon samples collected at the end of each experiment, are shown in Figures 2–10, 2–11, 2–12 and 2–13. Each spectrum shows a number of resonances in the range $\delta = 0.90$ to 1.90 ppm. These can be grouped into six sets of peaks, labelled I–VI in each case. Each set of peaks corresponds to resonances from deuterium atoms located in different positions within the exchanged methylcyclopentane molecules. The six possible locations for a deuterium atom in a methylcyclopentane molecule are shown in Figure 2–14, and the chemical shift, $\delta$, resulting from a D atom in each position is as listed in Table 2–5. The labels of the two sides of the ring, the 'open' side and the 'hindered' side are also shown in Figure 2–14. The hindered side refers to the deuterium atoms on the side of the ring cis to the methyl group, and the open side refers to the other side of the ring. The further splitting of each set of resonances is caused by isotopic shifts resulting from neighbouring deuterium atoms in the same molecule. These shifts are termed $\alpha$ for a shift caused by a D atom two bonds away, $\beta$ for a three bond shift and $\gamma$ for a four bond shift. The
Table 2-4: Product distributions and reaction rates from mass spectral analysis.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Pd1</th>
<th>Pd2</th>
<th>Pt1</th>
<th>Rh1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^3$ molecules/s/metal atom</td>
<td>0.55</td>
<td>1.7</td>
<td>6.9</td>
<td>7.2$^a$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% of species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$</td>
</tr>
<tr>
<td>$D_1$</td>
</tr>
<tr>
<td>$D_2$</td>
</tr>
<tr>
<td>$D_3$</td>
</tr>
<tr>
<td>$D_4$</td>
</tr>
<tr>
<td>$D_5$</td>
</tr>
<tr>
<td>$D_6$</td>
</tr>
<tr>
<td>$D_7$</td>
</tr>
<tr>
<td>$D_8$</td>
</tr>
<tr>
<td>$D_9$</td>
</tr>
<tr>
<td>$D_{10}$</td>
</tr>
<tr>
<td>$D_{11}$</td>
</tr>
<tr>
<td>$D_{12}$</td>
</tr>
<tr>
<td>$M_*$</td>
</tr>
</tbody>
</table>

$^a$ some slowing of rate was observed
Figure 2-6: Product distribution for experiment Pd1.
Figure 2–7: Product distribution for experiment Pd2.
Figure 2-8: Product distribution for experiment Pt1.
Figure 2–9: Product distribution for experiment Rh1.
Figure 2-10: 3D NMR spectrum of products of reaction Pd1.
Figure 2-12. 2D NMR spectrum of products of reaction Pt1.
Figure 2-13: 2D NMR spectrum of products of reaction Rh1.
Figure 2–14: The six positions for D atoms in methylcyclopentane.

Table 2–5: Chemical shifts due to deuterium atoms in methylcyclopentane.

<table>
<thead>
<tr>
<th>Position of D atom</th>
<th>δ /ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.84</td>
</tr>
<tr>
<td>II</td>
<td>1.72</td>
</tr>
<tr>
<td>III</td>
<td>1.50</td>
</tr>
<tr>
<td>IV</td>
<td>1.60</td>
</tr>
<tr>
<td>V</td>
<td>1.03</td>
</tr>
<tr>
<td>VI</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Figure 2–15: Illustration of isotopic shifts for a D atom in position IV in methylcyclopentane.

shifts are illustrated for a D atom in position IV in Figure 2–15, and the magnitude of the isotopic shifts, equally applicable to a D atom in any of the six positions are shown in Table 2–6. The isotopic shifts are additive, the net isotopic shift observed resulting from contributions from all neighbouring deuterium atoms. The values of the isotopic shifts listed were known approximately from previous 2D NMR study of cyclopentane [82], and other hydrocarbons [93].

<table>
<thead>
<tr>
<th>Shift</th>
<th>$-\Delta \delta$/ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>17 $\rightarrow$ 20</td>
</tr>
<tr>
<td>$\beta_{cis}$</td>
<td>7 $\rightarrow$ 9</td>
</tr>
<tr>
<td>$\beta_{trans}$</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{cis}$</td>
<td>1 $\rightarrow$ 3</td>
</tr>
<tr>
<td>$\gamma_{trans}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2–6: Isotopic shifts caused by neighbouring D atoms in methylcyclopentane.
2.7 Analysis of results

The peaks in the NMR spectra were integrated to determine the relative amounts of deuterium in each position in the methylcyclopentane molecules. The NMR spectrum is composed of resonances from deuterium incorporated into all product molecules. The origin of each deuterium resonance can be traced back to specific deuterium atoms, and used to obtain information on neighbouring deuterium atoms using the known values of chemical and isotopic shifts listed in Tables 2-5 and 2-6. The quantitative data obtained from experiment Pd1 is presented in Table 2-7.

The resonances due to deuterium in each of the six positions were identified, and then the area under each distinct peak or group of peaks was integrated in order to determine the relative amount of deuterium at each position. This is shown in the final column of Table 2-7. Similar analyses were performed for the other NMR spectra, and the quantitative information for all experiments is summarised in Table 2-8.

Since the isotopic shifts are most clearly resolved in the spectrum from experiment Pt1, Figure 2-12, this spectrum will be used to illustrate the analysis of the $^2$D NMR spectra.

In each of the six resonances, labelled I–VI, the peak at the highest $\delta$ is due to deuterium atoms in the named position, with no additional shift resulting from neighbouring deuterium atoms, $i.e.$ from the D$_1$-methylcyclopentane. In the example discussed, there are peaks shifted to lower $\delta$ within each set of resonances, resulting from the isotopic shifts due to neighbouring deuterium atoms. The shifts can be determined from the known isotopic shifts and by consideration of the location of the D atom in the methylcyclopentane molecule. In general, since $\gamma$ shifts are so small, they have been neglected, although their cumulative effect should be borne in mind.
Table 2-7: Analysis of deuterium in exchanged methylcyclopentanes from NMR analysis for experiment Pd1.

<table>
<thead>
<tr>
<th>Position of D atom</th>
<th>Isotopic shift (δ/ppm)</th>
<th>-Δδ/ppb</th>
<th>Relative % D in each position</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.85</td>
<td>0</td>
<td>7.1 13.4</td>
</tr>
<tr>
<td></td>
<td>1.81</td>
<td>36</td>
<td>6.3</td>
</tr>
<tr>
<td>II</td>
<td>1.72</td>
<td>0</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>1.71</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td>20</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>1.66</td>
<td>52</td>
<td>5.1</td>
</tr>
<tr>
<td>III</td>
<td>1.50</td>
<td>0</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>1.48</td>
<td>20</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>53</td>
<td>5.3</td>
</tr>
<tr>
<td>IV</td>
<td>1.60</td>
<td>0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>1.59</td>
<td>16</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>55</td>
<td>5.0</td>
</tr>
<tr>
<td>V</td>
<td>1.03</td>
<td>0</td>
<td>7.5 13.4</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>32</td>
<td>5.9</td>
</tr>
<tr>
<td>VI</td>
<td>0.95</td>
<td>0</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>20</td>
<td>2.6 20.3</td>
</tr>
<tr>
<td></td>
<td>0.91</td>
<td>41</td>
<td>15.9</td>
</tr>
</tbody>
</table>
Table 2–8: NMR analysis of groupings of deuterium atoms in exchanged methylcyclopentanes.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Average</th>
<th>Pd1</th>
<th>Pd2</th>
<th>Pt1</th>
<th>Rh1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>Isotopic</td>
<td>Percentage of deuterium in each group</td>
<td>-Δδ/ppb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>of D atom</td>
<td>Shift</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>7.1&lt;sup&gt;a&lt;/sup&gt; 7.1 5.4 11.9</td>
<td>30 6.3 5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.6&lt;sup&gt;a&lt;/sup&gt; 5.9 13.7 18.1</td>
<td>37 5.1 11.3 8.6 4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>11.9 5.7 12.9 16.7</td>
<td>44 5.3 12.1 8.9 5.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>8.0&lt;sup&gt;a&lt;/sup&gt; 4.9 7.4 4.5</td>
<td>42 5.0 20.9 11.0 6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>7.5 3.3 5.0 4.6</td>
<td>32 5.9 10.6 7.2 6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12&lt;sup&gt;b&lt;/sup&gt; 1.8 1.3 1.8 2.4</td>
<td>33 2.6 2.5 2.6 5.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 15.9 14.4 9.3 13.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M&lt;sub&gt;VI&lt;/sub&gt;</td>
<td>2.7 2.3 2.0 2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> includes partially resolved resonances due to singly exchanged molecules

<sup>b</sup> measured only for Pt1 and assumed to hold for the other experiments
With reference to Figures 2-14 and 2-15, it can be seen that deuterium in position I may experience isotopic shifts due to up to seven \( \beta \) shifts, from up to three D atoms located in position VI, and up to two in each of positions II and V. Since a deuterium atom at position I is attached to a tertiary carbon atom, there can be no neighbouring D atoms to give an \( \alpha \) shift. Hence the shifted component of the peak must be due to a number of \( \beta \) neighbours.

In position II, deuterium may experience isotopic shifts due to a neighbouring D atom in position V giving an \( \alpha \) shift, and up to three \( \beta \) shifts from deuterium atoms at positions I, III and IV. This will give a range of net shifts from \( \sim 8 \) ppb for only one \( \beta \) shift to \( \sim 42 \) ppb for D in position II with one \( \alpha \) and three \( \beta \) neighbours. In the Pt1 spectrum, most of the deuterium in position II has neighbouring D atoms, as shown by the intensity of the shifted peaks. The unshifted resonance is resolved only as a shoulder of the neighbouring resonance, and is included in that integral.

For deuterium in position III, there can be one deuterium atom at position IV giving an \( \alpha \) shift, and up to four \( \beta \) shifts from deuterium atoms in positions II, V and the other III and IV positions. The spectrum shows most of the resonance to be slightly shifted, and some to be highly shifted at \(-\Delta \delta = 34.6 \) ppb.

For position IV, the possible isotopic shifts are very similar to those for deuterium in position III. However, the integrated area for peak IV shows that overall, less deuterium is incorporated at this position as compared with the amount at position III, on the other side of the ring. The relative intensities of the peaks in groups III and IV are reversed. A deuterium atom in position V can experience similar shifts to one in position II, with an additional \( \beta \) shift possible due to deuterium in position I. The majority of deuterium in position V appears in the peak shifted \( \sim 32 \) ppb.

The resonance due to deuterium in position VI, the methyl group, shows splitting into four separate peaks. Deuterium in position VI can experience up to two \( \alpha \) shifts and one \( \beta \) shift from deuterium in position I. The largest isotopic shift observed in the spectrum, of \(-\Delta \delta = 56 \) ppb, must be due to two \( \alpha \)
and one $\beta$ shift. The peaks can be assigned to one exchanged methyl D atom at $\delta = 0.96$ ppm, with the peaks shifted by $-\Delta \delta = 12$ ppb, 33 ppb and 56 ppb to a neighbouring D atom at position I, two neighbours, one at position I and one in position II, and to the fully exchanged methyl group plus D at position I respectively. By far the greatest intensity within the VI resonance is in the highly shifted peak, indicating completion of methyl group exchange along with exchange at position I is the most favourable process.

The spectra from the other experiments are broadly similar to the one discussed above, but show variation in the relative intensities of the resonances. None of the other spectra show such well resolved resonances for singly exchanged molecules in positions I–IV, but for experiment Pt1, the methyl group resonance is split into four components. The spectrum from experiment Pd1 shows perhaps the best resolution in the resonances from deuterium atoms located in positions II–IV, where the narrow peak at the highest $\delta$ in each group of peaks due to singly exchanged methylcyclopentane is clearly discernible. However, they were not well enough separated from the neighbouring peaks to be analysed separately.

The quantitative NMR data listed in Table 2–8 was then used to investigate the relative amount of exchange of each of the twelve hydrogen atoms in a methylcyclopentane molecule.

A random exchange of deuterium into a methylcyclopentane molecule would result in $1/12$ or 8.3% of the deuterium being located at position I, 16.7% at each of positions II–IV, and 25% at position VI for the 1, 2, and 3 hydrogen atoms at these positions respectively.

In order to compare the observed exchange with the random exchange described above, the observed amount of deuterium for each position, as listed in Table 2–8, was ratioed against the equivalent amount expected in a random exchange. This would give a ratio of unity for each position if the exchange was completely random. Values greater than one indicate favourable exchange into that position, whereas values below one suggest
poor exchange. The relative amounts of deuterium incorporated into the molecule at each position are listed in Table 2-9.

From the quantitative NMR data, additional information concerning the extent of exchange in the methyl group, position VI, could be calculated. Poorest exchange into the methyl group was observed over platinum, although the relative exchange into the methyl group was less than one for all experiments, as shown in Table 2-9.

<table>
<thead>
<tr>
<th>Table 2-9: Relative exchange at each position.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
</tr>
<tr>
<td>Position</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>I</td>
</tr>
<tr>
<td>II</td>
</tr>
<tr>
<td>III</td>
</tr>
<tr>
<td>IV</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>VI</td>
</tr>
</tbody>
</table>

The methyl group resonance was always resolved into three component peaks, and four in the case of experiment Pt1. The mean number of deuterium atoms in exchanged methyl groups, MVI, was determined for each experiment, and these values are shown in the final line in Table 2-8. MVI was calculated by dividing the total percentage of deuterium in position VI by the sum of the individual peak percentages / the number of D neighbours. For experiment Pt1, this gives

\[
M_{VI} = \frac{1.2 + 1.8 + 2.6 + 9.3}{1.2 + 1.8 + (2.6/2) + (9.3/3)} = 2.0
\]

Comparing the values of MVI with the figures for the relative exchange into the methyl group in Table 2-8, it is apparent that there is poor overall exchange into the methyl group in all experiment. The MVI value of over 2 indicates considerable exchange into the methyl groups that did exchange.
The quantitative NMR data summarised in Table 2–8 can also be used to determine the relative amounts of methylcyclopentane exchanged on the open side, the hindered side and on both sides. The resonances in the 2D NMR spectra are generally composed of two or more distinct peaks. These can be integrated, and considering the isotopic shifts in Table 2–6, the peaks can be assigned as the least shifted, i.e. at highest δ, to molecules only exchanged on one side, and the highly shifted (lowest δ) peak to molecules exchanged on both sides, with a large contribution to the shift from an α D atom shift.

For experiment Pt1, using the relative values for the less and more highly shifted resonances, Table 2–8, the fractions can be calculated as follows. For deuterium in position II, the fraction of molecules exchanged on both sides is $8.6/(8.6 + 13.7) = 0.39$. Similarly, for deuterium incorporated at position III, the fraction exchanged on both sides is $8.9/(8.9 + 12.9) = 0.41$. Hence, the average fraction of molecules exchanged on the open side and also exchanged on the hindered side is $(0.39 + 0.41)/2 = 0.40$. For deuterium on the hindered side, the fraction at position IV also exchanged on the open side is $11.0/(11.0 + 7.4) = 0.60$, and similarly for position V is $7.2/(7.2 + 5.0) = 0.59$. This gives a mean fraction of $(0.60 + 0.59)/2 = 0.60$ of molecules exchanged on the hindered side also exchanged on the open side.

The ring positions II–V can be used for this calculation since deuterium at each of these positions can have an α neighbour, contributing to the highly shifted peak. Data for deuterium at positions I and VI cannot be considered as only β (and γ) shifts affect position I, and anything relating to position VI refers to the methyl group and not to exchange in the ring.

If $f_o$, $f_h$ and $f_b$ represent the fractions of molecules exchanged on the open side only, the hindered side only and on both sides, then

$$f_o + f_h + f_b = 1$$

$$\frac{f_b}{f_o + f_b} = 0.40$$

$$\frac{f_b}{f_h + f_b} = 0.60$$
and from these equations, it can be determined that \( f_o = 0.47 \), \( f_h = 0.21 \) and \( f_b = 0.32 \). Similar fractions can be determined for other experiments, and these are summarised in Table 2–10.

Again, further information can be determined relating to methyl group exchange. Of the molecules exchanged on both sides, given by fraction \( f_b \) some will be exchanged in the methyl group and some will not. The values of \( MVI \) listed in Table 2–8 give an indication of the extent of exchange into the methyl group.

Now, \( f_b f_{bm} \) is used to represent the fraction of molecules exchanged on both sides of the ring and in the methyl group, and \( f_b (1 - f_{bm}) \) represents those molecules exchanged on both sides but not in the methyl group.

The fractions \( f_b f_{bm} \) and \( f_b (1 - f_{bm}) \) can be estimated using the mass spectral data in Table 2–4. The minimum values can be determined from the fraction of the \( D_{10} - D_{12} \) deuteroproducts since these molecules must be exchanged on both sides and in the methyl group. Again for experiment Pt1, this gives \( f_b f_{bm} = (0.5 + 1.0 + 1.7)/(100 - 82.5) = 0.18 \), and \( f_b (1 - f_{bm}) = f_b - f_b f_{bm} = 0.32 - 0.18 = 0.14 \). The estimate of the fraction \( f_b f_{bm} \) is an under estimate since some molecules with less than ten deuterium atoms will be partially exchanged on both sides and in the methyl group. The values determined for all experiments are listed in Table 2–10.

### 2.8 Discussion

The figures in Table 2–10 indicate that in all experiments there is greater incorporation of deuterium into positions IV and V than into positions II and III. The two experiments over the palladium catalyst, Pd1 at 293K and Pd2 at 333K, show that the increase in temperature leads to a higher proportion of molecules exchanged on both sides. Table 2–9 shows that in all experiments, exchange into positions II and III is greater than the amount from a purely random exchange, and, conversely, a smaller amount than

57
that from random exchange is incorporated into positions V and VI. The relative amounts incorporated into positions I and IV is variable and will be discussed later. The pattern of exchange, from Table 2–9 shows generally that most deuterium is exchanged on the open side of the molecule (positions I–III) followed by the hindered side (positions IV and V) with the smallest amount being in the methyl group (position VI). The results for each metal are discussed individually below, and general conclusions are presented in Section 2.9.

Table 2–10: Fractions of methylcyclopentanes exchanged in different ways.

<table>
<thead>
<tr>
<th>Description</th>
<th>Pd1</th>
<th>Pd2</th>
<th>Pt1</th>
<th>Rh1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Posn. II exch. both sides</td>
<td>0.22</td>
<td>0.66</td>
<td>0.39</td>
<td>0.21</td>
</tr>
<tr>
<td>Posn. III exch. both sides</td>
<td>0.31</td>
<td>0.68</td>
<td>0.41</td>
<td>0.24</td>
</tr>
<tr>
<td>Posn. IV exch. both sides</td>
<td>0.38</td>
<td>0.81</td>
<td>0.60</td>
<td>0.57</td>
</tr>
<tr>
<td>Posn. V exch. both sides</td>
<td>0.44</td>
<td>0.76</td>
<td>0.59</td>
<td>0.58</td>
</tr>
<tr>
<td>open side only, f_o</td>
<td>0.53</td>
<td>0.28</td>
<td>0.47</td>
<td>0.66</td>
</tr>
<tr>
<td>hindered side only, f_h</td>
<td>0.28</td>
<td>0.16</td>
<td>0.21</td>
<td>0.14</td>
</tr>
<tr>
<td>both sides, f_b</td>
<td>0.19</td>
<td>0.56</td>
<td>0.32</td>
<td>0.20</td>
</tr>
<tr>
<td>both sides without methyl, f_b(1-f_mb)</td>
<td>0.04</td>
<td>0.09</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>both sides with methyl, f_b(f_mb)</td>
<td>0.15</td>
<td>0.47</td>
<td>0.18</td>
<td>0.10</td>
</tr>
</tbody>
</table>

2.8.1 Palladium

The main feature of the mass spectral results from both palladium experiments are the clear breaks in the product distributions after the D_4, D_8 and D_12 methylcyclopentanes, similar to the distributions observed by Burwell, Figure 2–4 [76]. Experiment Pd2 also shows a minor maximum at D_2. As discussed earlier, the maximum at D_4 was assigned to arise from exchange
of the hydrogen atoms on the hindered side of the ring via the $\alpha\beta$ process, following from initial adsorption on that side of the ring. Exchange does not propagate easily into the methyl group from this group of hydrogen atoms, as an $\alpha\gamma$ intermediate would be involved. A study of the exchange of 2,2-dimethylpropane with deuterium has shown that $\alpha\gamma$ species are not readily formed on palladium [85].

Molecules which adsorb on the open side of the ring can exchange the ring hydrogen atoms easily via the $\alpha\beta$ process, and this can propagate the exchange into the methyl group to give the maximum observed at C$_6$H$_4$D$_8$.

The third maximum at the fully exchanged molecule indicates that some mechanism occurs readily, allowing the molecule to turnover on the catalyst surface to exchange all hydrogen atoms. This is reflected in the results in Table 2–10. Also, for both experiments over palladium, Table 2–10 shows that of the molecules exchanged on both sides, most are also exchanged in the methyl group, with only a small proportion not also exchanged in the methyl group. This is in marked contrast to the experiments over the other metals, indicating that propagation of exchange into the methyl group occurs most readily on palladium.

The relative exchange into each position varied with the temperature of the experiment, as shown in Table 2–9. In experiment Pd1, at 293K, preferential exchange occurred on the open side of the ring, with similar extents of exchange on the hindered side and in the methyl group. However, at 333K, preferential exchange at position IV, on the hindered side, was observed, clearly shown by the large peak in Figure 2–11.

### 2.8.2 Platinum

Results for experiment Pt1 show that the extent of incorporation of deuterium decreases in the order open side $>$ hindered side $>$ methyl group. The mass spectral product distribution, Figure 2–8, shows distinct breaks after C$_6$H$_7$D$_5$ and C$_6$H$_4$D$_8$ and a maximum at C$_6$D$_{12}$. The maximum at D$_5$
was not observed for the other metals, and results from the exchange of the five hydrogen atoms on the open side of the ring *via* the $\alpha\beta$ process.

The large $D_1$ peak in the mass spectral distribution indicates that there is considerable stepwise exchange over platinum, in addition to the multiple exchange that gives the more highly deuterated products. The molecules containing single deuterium atoms are exchanged at positions II–VI, as shown by the shoulders in the NMR spectrum, Figure 2–12, and from comparison with an NMR spectrum recorded at higher field from the products of a similar reaction over Pt/Al$_2$O$_3$ [94]. The U-shaped distribution of isotopic products observed in Figure 2–8 is typical of reactions over platinum [62, 95-97].

### 2.8.3 Rhodium

The product distribution for experiment Rh1, Figure 2–9 shows similar amounts of the $D_1$–$D_8$ products, with a large peak at $D_2$, and decreasing amounts of $D_9$–$D_{12}$. Table 2–9 shows that there is considerable open side exchange, the least hindered side exchange of all experiments, and the highest extent of exchange into the methyl group. For molecules initially exchanged in positions II and III, on the open side, less turnover of the molecule occurs than for the equivalent reaction over platinum.

The NMR spectrum from the products of reaction Rh1, Figure 2–13 was less intense than the other NMR spectra, and consequently resonances were less well resolved, and some groupings could not be clearly identified.

The break in the product distribution after $D_8$ again results from multiple exchange, *via* the $\alpha\beta$ process, of the open side and methyl hydrogen atoms. The decrease in the rate of reaction for experiment Rh1, as seen in the rate plots, suggests that self-poisoning of the reaction was occurring. This type of behaviour has been reported for hydrocarbons containing quaternary carbon atoms, at 423K, over Rh/SiO$_2$ [86].
A possible explanation for the self-poisoning of the reaction over rhodium is that a strongly held species is formed on the surface which undergoes carbon–carbon bond rupture in preference to desorption. Rhodium has been observed to catalyse carbon–carbon bond rupture of cyclopentane at 340K [86] and is also known to cause hydrogenolysis [98].

2.9 Conclusions

The experiments discussed in this Chapter have confirmed previously established mechanisms of methylcyclopentane exchange, and the use of 2D NMR spectroscopy has allowed quantification of the deuterium incorporated into the different locations in the methylcyclopentane molecules. The mass spectral product distributions showed the characteristic patterns for exchange over each metal, these being the typical U-shaped distribution for platinum with maxima at D$_1$, D$_5$ and D$_{12}$ products, extensive exchange over palladium, and relatively uniform exchange over rhodium with only limited exchange beyond D$_9$.

Methylcyclopentane has proved to be a suitable molecule for 2D NMR study in that a distinct resonance was observed for deuterium in each different environment within the methylcyclopentane molecules. Hence, each peak in the spectra could be assigned to deuterium atoms in particular locations, and information on their neighbouring deuterium atoms determined.

For all metals, the results are consistent with the main mechanism of exchange being multiple exchange \textit{via} the $\alpha\beta$ mechanism, involving interchange between adsorbed alkyl and alkene species on the surface. These surface intermediates are illustrated in Figure 2–16. (a) shows adsorption of a methylcyclopentane molecule on the surface to form an arbitrarily chosen alkyl species, and (b) shows interconversion between an alkyl species and an alkene species to produce an exchanged alkyl species. This allows propagation of exchange around each set of hydrogen atoms, giving up to
Figure 2–16: Illustration of proposed mechanisms of methylcyclopentane exchange. The species in (a), (b) and (c) are horizontal species and (d) is vertically adsorbed.
the D₄ product for molecules initially adsorbed on the hindered side of the ring, and up to D₈ products for those initially adsorbed on the open side. Exchange propagates from the open side into the methyl group via the αβ mechanism involving a 1,2-diadsorbed species or an exocyclic alkene species. This is illustrated in Figure 2–16 (c).

For propagation of exchange beyond D₈, there must be a mechanism other than the αβ mechanism, allowing the adsorbed methylcyclopentane molecule to turnover on the surface. Figure 2–16 (d) illustrates this. This may involves a vertically adsorbed 'alkene' species, held on the surface between positions II and III, directly across the ring from the methyl group. The two experiments over palladium suggest that there is an increase in turnover of the molecule with temperature, leading to more highly exchanged molecules. Also, molecules initially adsorbed on the hindered side turned over more easily than those initially adsorbed on the open side. Most turnover was observed for palladium, and the least on rhodium, suggesting that the vertical 'alkene' species is least tightly held on the palladium surface. The efficiency of multiple exchange is greatest for palladium and poorest for rhodium.

Integration of the ²D NMR spectra allowed quantification of deuterium in each of the six positions in methylcyclopentane, and also determination of the relative amounts exchanged on either or both sides of the ring. The greater amounts exchanged on the open side than on the hindered side suggest that initial adsorption on the catalyst surface to form an alkyl species at positions I, II and III is easier than at positions IV and V. This probably results from steric hindrance due to the methyl group, resulting in a less negative heat of adsorption for alkyl species at positions IV and V. Consequently, the αβ mechanism leads to greater exchange on the open side than on the hindered side.

Exchange into the methyl group was less than into both sides of the ring. The methyl hydrogen atoms are in the same 'set' of hydrogen atoms as those on the open side of the ring. Propagation of exchange from these
ring positions into the methyl group is not as efficient as exchange via the \( \alpha \beta \) mechanism between the five open side ring positions, but once started, tends to be efficient, again propagating via the \( \alpha \beta \) mechanism with rotation about the ring/methyl C–C bond. As noted earlier, minor maxima at D\(_2\) were observed in experiments Pd2 and Rh1, and probably result from pairwise exchange of hydrogen atoms with a D\(_2\) molecule from initial adsorption of methylcyclopentane as an \( \alpha \beta \) diadsorbed or alkene species [99]. This type of behaviour has been described recently for cyclopentane exchange over Ni/SiO\(_2\) [100].
3.1 Infrared Spectroscopy

Infrared spectroscopy has been used to study adsorption on surfaces since the first transmission IR spectra of physisorbed molecules were recorded in the late 1940s [101]. In the 1950s, techniques were developed to facilitate study of molecules chemisorbed on supported metal catalysts. Such catalysts lend themselves to transmission infrared spectroscopy on account of their high surface area and hence good spectroscopic sensitivity. The first reported transmission infrared studies on catalyst surfaces were by Eischens and colleagues in the mid 1950s [102, 103].

Transmission Infrared Spectroscopy has remained one of the most widely used and successful forms of infrared spectroscopy for recording spectra of adsorbates on supported metal catalysts. Indeed, it is probably the single most important technique of all in the study of surface species, and many review articles on transmission infrared spectroscopy have been published [104-108]. Due to the advent of Fourier Transform instrumentation,
new techniques including Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS), Photoacoustic spectroscopy (PAS), Attenuated Total Reflectance (ATR), Reflection Absorption Infrared Spectroscopy (RAIRS) and Infrared Emission Spectroscopy (IRES) have been developed, although the detected signal is smaller with these new techniques than with conventional transmission infrared spectroscopy. Today, transmission infrared and DRIFTS are the most widely used forms of infrared spectroscopy in catalyst research.

Infrared spectroscopy is predominantly applied to supported metal catalysts, and only very recently (in the late 1980s) have technological developments in reflection infrared experiments been sufficient to allow satisfactory Reflection Absorption Infrared (RAIRS) spectra of hydrocarbons adsorbed on metal single crystals to be obtained, although earlier work was done on less well defined evaporated metal films. A complementary approach to adsorption on poorly defined supported metal catalysts is the use of single crystal metal surfaces, offering a greater insight into the structure and bonding of molecules on well defined surfaces. Both such studies have been undertaken in this Thesis in order to investigate the adsorption of small cyclic hydrocarbon molecules on metal surfaces. In this Chapter, DRIFTS and Transmission infrared experiments are described, and RAIRS experiments are discussed in Chapter 4.

3.2 The Physical Basis of Infrared Spectroscopy

Infrared radiation is usually described as the electromagnetic radiation with frequency between \( \sim 10000 \) and \( 20\text{cm}^{-1} \). This range is generally sub-divided into the near infrared (\( >4000\text{cm}^{-1} \)), the mid-infrared (\( 4000 \) - \( 400\text{cm}^{-1} \)) and the far-infrared (\( <400\text{cm}^{-1} \)). Vibrational frequencies within molecules and of metal-adsorbate bonds coincide with the frequency of infrared radiation. These vibrations interact with the infrared beam and absorb certain fre-
frequencies of radiation giving rise to characteristic absorption bands in the infrared spectrum. Hence, provided the necessary selection rules are satisfied, infrared absorption bands can be observed.

Infrared spectra can be recorded in situ for solids, liquids, gases and adsorbed species. Bands in an infrared spectrum can be assigned from analysis of their frequencies, with a knowledge of characteristic ‘group’ frequencies of functional groups or by comparison with the vast ‘library’ of reference spectra which has been established.

In the gas phase, an atom has three kinetic degrees of freedom. Correspondingly, a non-linear gas phase molecule containing $n$ atoms possesses $3n$ degrees of freedom, of which 3 are translational, 3 are rotational and $3n-6$ are vibrational. For an $n$ atom linear molecule, there are 3 translational, 2 rotational and $3n-5$ vibrational degrees of freedom. For each non-degenerate vibrational degree of freedom, there is a normal mode where all atoms vibrate at the same frequency and pass through their equilibrium positions together. Adsorption of an $n$ atom molecule on a surface creates an additional $3n$ degrees of freedom in the system as a whole. The strength of the coupling between the vibrations of the adsorbed species and the lattice modes of the substrate will depend on the relative frequencies of both these vibrations. An example of strong coupling between the adsorbate and substrate vibrations is that of the surface hydroxyl groups on silica and the lattice Si-O vibrations. For an adsorbate containing light atoms on a metal surface containing heavy atoms, the metal-metal vibrations will be at much lower frequency than those of the adsorbate, and each will have little effect on the other i.e. coupling will be weak.

When a molecule is loosely held to a metal surface i.e. physically adsorbed, at least one translational degree of freedom of the free molecule must be converted to a metal-adsorbate vibration. The other translations and rotations may be retained. For a molecule more strongly held on a metal surface, i.e. chemisorbed, where it is not free to move, the translational and rotational degrees of freedom become ‘frustrated’ and may become
vibrational modes resulting from the new chemical bonds to the metal surface. These 'external' modes (which are related to the translations and rotations of the free molecule) can then mix with the 'internal' modes of the free molecule of the same symmetry which may alter the frequencies of the absorption bands.

Depending on the symmetry properties of the adsorption site, fewer than the anticipated $3n$ bands may appear in the infrared spectrum. This is illustrated for the adsorption of one of the most common adsorbates, CO, adsorbed on 4-fold and 2-fold sites on a typical metal surface e.g. the (100) surface in Figure 3-1. The symmetry of any molecule can be described by the point group to which it belongs [109]. Each vibration can then be characterised by a symmetry species from the appropriate point group character table.

An example of the symmetry change on adsorption is the adsorption of CO in two different symmetry sites on a metal surface. For CO linearly adsorbed in an 'on-top' site of $C_{4v}$ symmetry, four bands would be expected, whereas for CO adsorbed in the two-fold 'bridging' site of $C_{2v}$ symmetry, six bands are anticipated. However, in practice, $\nu_1$, the $C=O$ stretching vibration mixes with $\nu_2$, the frustrated translation in the z-direction and the frequencies of both are altered from those of the pure $C=O$ stretching vibration and the M-CO stretch. It is apparent from Figure 3-1 that two different sets of infrared bands would be expected for CO adsorbed linearly in an 'on-top' position and in a two-fold 'bridging' position. The degeneracy of the frustrated translations and rotations is lifted for CO in the bridging site. However, as with all spectroscopic techniques, there are selection rules which must be obeyed in order for bands to be observed. Only vibrations of suitable symmetry species are observable, and for IR spectroscopy used to observe an adsorbate on a metal surface, usually only totally symmetric modes are allowed. This is further discussed in the next Section.

The lowering of the symmetry of the CO molecule upon adsorption is typical of any adsorption process [110]. An adsorbed species can only possess
Figure 3–1: Illustration of adsorption of CO on a metal surface (left) linearly bonded with 4-fold rotational symmetry, and (right) bridge bonded with 2-fold rotational symmetry.
rotation axes and mirror planes normal to the metal surface. In practice, the point groups allowed for surface species [111] are:

\[ C_1, C_2, C_2', C_3, C_3', C_4, C_4', C_6 \text{ and } C_{6v} \]

The effect of adsorption on a Pt(111) surface on the infrared spectrum of CO is shown in Figure 3–2. Spectrum (a) shows the infrared spectrum for gas phase CO and (b) shows the reflection absorption infrared spectrum of CO adsorbed on a Pt(111) single crystal surface.

Figure 3–2: IR spectra of (a) gas phase CO and (b) CO adsorbed on a Pt(111) surface, from [112].
The gas phase spectrum shows many bands centered on 2143 cm\(^{-1}\) including rotational fine structure (closely spaced bands) which arises from transitions between the quantised rotational energy levels. At room temperature, only the lowest vibrational energy level, \(\nu = 0\), is significantly populated for transitions > 1000 cm\(^{-1}\), and absorption of a quantum of infrared radiation leads to a transition to an excited vibrational level. Only transitions with \(\Delta \nu = 1\) are allowed and the dominant transition is from \(\nu = 0\) to \(\nu = 1\). The rotational fine structure is lost on adsorption as described above, and the RAIRS spectrum shows two bands corresponding to CO adsorbed in two sites of different symmetry, in 'on-top' and 'bridging' positions. The width of absorption bands is also increased due to inhomogeneous broadening and the decreased lifetime of the vibrationally excited state. The bands are shifted downwards (to lower \(\bar{\nu}\)) from the position of the free molecule. On Pt(111) there are clearly two absorption bands separated by \(\sim 240\) cm\(^{-1}\), due to the \(\nu_1\) vibrations of CO in different sites. The geometry of an adsorbate can often be deduced from observation of bands in the IR spectrum.

Following studies of CO adsorption, the adsorption of various hydrocarbon molecules on metal surfaces has and continues to be widely studied. This has led to the characteristic 'group' frequencies mentioned briefly earlier. Some typical hydrocarbon vibrations and their vibrational frequencies are shown in Tables 3-1 and 3-2.

Hence, an infrared spectrum of an adsorbate can be readily interpreted with a knowledge of these group frequencies and with information determined from single crystal work and from comparison with organometallic compounds. Minor variations in the quoted frequencies arise as a result of local differences in the environment of the adsorption site.
Table 3–1: Some hydrocarbon vibrations and their typical group frequencies, from[106].

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Description</th>
<th>Notation</th>
<th>Frequency/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(≡\text{C}–\text{H})</td>
<td>Alkyne CH stretch</td>
<td>(ν (\text{CH}))</td>
<td>3300</td>
</tr>
<tr>
<td>(\text{C}≡\text{C})</td>
<td>Alkene CH stretch</td>
<td>(ν (\text{CH}_2))</td>
<td>3020</td>
</tr>
<tr>
<td>(−\text{C}–\text{H}–\text{H})</td>
<td>Asymmetric CH(_3) stretch</td>
<td>(ν (\text{CH}_3)) asym.</td>
<td>2960</td>
</tr>
<tr>
<td>(\text{C}–\text{H}–\text{H})</td>
<td>Asymmetric CH(_2) stretch</td>
<td>(ν (\text{CH}_2)) asym.</td>
<td>2925</td>
</tr>
<tr>
<td>(−\text{C}–\text{H}–\text{H})</td>
<td>Symmetric CH(_3) stretch</td>
<td>(ν (\text{CH}_3)) sym.</td>
<td>2870</td>
</tr>
<tr>
<td>(\text{C}–\text{H}–\text{H})</td>
<td>Symmetric CH(_2) stretch</td>
<td>(ν (\text{CH}_2)) sym.</td>
<td>2850</td>
</tr>
<tr>
<td>(\text{C}–\text{C})</td>
<td>C-C stretch</td>
<td>(ν (\text{C}-\text{C}))</td>
<td>900(^a)</td>
</tr>
</tbody>
</table>

\(^a\) from [107]
Table 3-2: Some hydrocarbon vibrations and their typical group frequencies contd., from[106].

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Description</th>
<th>Notation</th>
<th>Frequency/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv\equiv$</td>
<td>C=C stretch</td>
<td>$\nu$(C-C)</td>
<td>1650</td>
</tr>
<tr>
<td>$\equiv$</td>
<td>CH₂ deformation</td>
<td>$\delta$(CH₂)</td>
<td>1465</td>
</tr>
<tr>
<td>$\equiv$</td>
<td>Asymmetric CH₃ deformation</td>
<td>$\delta$(CH₃) asym.</td>
<td>1450</td>
</tr>
<tr>
<td>$\equiv$</td>
<td>Symmetric CH₃ deformation</td>
<td>$\delta$(CH₃) sym.</td>
<td>1375</td>
</tr>
<tr>
<td>$\equiv$</td>
<td>In-plane deformation</td>
<td>$\delta$ i.p.</td>
<td>1410</td>
</tr>
<tr>
<td>$\equiv$</td>
<td>Out of plane deformation</td>
<td>$\delta$ o.p.</td>
<td>890</td>
</tr>
</tbody>
</table>
3.3 Selection Rules

The fundamental selection rule for a vibration to be infrared active is that it produces a dipole change. It is the interaction of an oscillating dipole with the electromagnetic radiation that leads to absorption.

For molecules adsorbed on a metal surface, there is a further selection rule, known as the 'metal surface selection rule' (MSSR), which states that only modes which have vibrational dipole moments perpendicular to the metal surface will have measurable intensities [113, 114]. In practice, this generally means that only totally symmetric modes are infrared active. In the CO example discussed above, this means that only the $\nu_1$ and $\nu_2$ vibrations can be observed with IR. The underlying physical reason for the existence of the metal surface selection rule is because the metal modifies the way in which an adsorbed molecule interacts with the infrared radiation. A perfect metal has high electron mobility and good electrical conductivity in the infrared region. The tangential component of the electric field vector, $E$, must be continuous across the metal surface. Inside a perfect conductor, $E$ must be zero. In reality, this means that the electric field is perpendicular to the surface of a perfect conductor.

For an oscillating dipole on the metal surface, generated by the absorption of an infrared photon, an 'image' dipole is created below the metal surface, resulting from the response of the metal conduction electrons to the field established by the adsorbed dipole. This is illustrated schematically in Figure 3–3 for a dipole adsorbed either perpendicular or parallel to a flat metal surface.

Figure 3–3 shows that a vibrational dipole oscillating perpendicular to the metal surface is reinforced by its image, whereas a dipole oscillating parallel to the surface is effectively cancelled by its image. The long range electromagnetic field of the infrared radiation cannot distinguish between the real dipole and its image and so interacts with the sum of their dipole
fields. The actual result of this is that in the limit, vibrations perpendicular to the surface are enhanced by a factor of two and those parallel to the surface are cancelled. Maximum absorption occurs with the infrared beam polarised perpendicular to the surface at near grazing incidence [113].

The above illustration was for a flat metal surface, but the metal surface selection rule has been shown to apply to metal particles down to approximately 2nm diameter [114, 115]. The point at which the metal surface selection rule no longer holds i.e. for small particles has been investigated. The bending of electric field lines by a metal particle (idealised as a sphere) is illustrated in Figure 3–4. A metal particle, or sphere bends the electric field lines such that they intersect the surface perpendicularly. Depending on the size of the particle, the bending of the electric field lines in the region of adsorbed particles is slightly different. $E$ can be resolved into a radial component, $E_r$, and a tangential (parallel) component, $E_t$. A large particle
can bend the field lines enough for them to be perpendicular to the particle surface, and thus there is no tangential component of \( E \). However, small particles, where the curvature of the surface is similar to the wavelength of the radiation, are not able to bend the electric field lines to be normal to the surface. In this case, the tangential component of \( E \) is significant, and \( E_r \) is reduced. The relative ratio of \( E_r \) to \( E_t \) determines the extent of the interaction with a vibrating dipole. The metal surface selection rule holds as long as the adsorbate sees no tangential component of \( E \), i.e. the particle is large enough to bend the electric field lines to be perpendicular to the surface over typical adsorbate distances from the surface. The field lines must remain perpendicular over the distance from the surface in which the adsorbate lies, typically within \( 0.2 \rightarrow 0.3 \text{nm} \) of the surface for chemisorbed species. Hence, the MSSR works out to be only for particles above 2nm diameter. This ties in conveniently with infrared work on supported metal catalysts which typically have particle sizes above 2nm diameter. EuroPt-1 particles have a distribution in particle size from \( 0.9 \rightarrow 3.5 \text{nm} \) with \( 75\% \leq 2\text{nm} \). The recognition, understanding and appreciation of the metal surface selection rule has been crucial in the understanding of infrared spectra of adsorbed species on metal surfaces.
3.4 The application of Transmission IR and DRIFTS

Infrared radiation can interact with a high surface area catalyst sample and adsorbate in a number of ways. These include transmission, absorption and reflection. Reflection from the topmost surface of the sample, where the angle of incidence and the angle of reflection are equal is known as (specular) Fresnel reflection, or as specular reflection. Reflection can also occur from the surfaces of particles in the bulk of the sample. When this is from surfaces not parallel to the topmost layer, it is known as diffuse Fresnel reflection. Regular Fresnel reflection also occurs from the surfaces of particles in the bulk aligned parallel to the topmost layer. The amount of Fresnel reflection depends on properties of the catalyst — the refractive index and the index of absorption, and also the angle of incidence of the infrared beam.

Some of the main forms of interaction of radiation with a catalyst are shown in Figure 3–5 (RAIRS is generally applied to single crystal model catalysts). In this Chapter, transmission and diffuse reflectance are used to study adsorption on a supported metal catalyst, and in Chapter 4, Reflection Absorption Infrared Spectroscopy is used to study adsorption on a Pt(111) single crystal.

The observation of absorption bands using DRIFTS or transmission infrared spectroscopy does not imply that the species giving rise to these vibrations are the catalytically active species. Their catalytic activity must be substantiated by other means, such as parallel behaviour in the gas phase. The formation or decay of bands can be monitored with exposure to adsorbate, as a function of time or with increasing temperature. Isotopic exchange experiments can be used to probe the intermediates adsorbed on the catalyst surface. Infrared spectroscopy alone cannot prove that the observed species on the surface is / are catalytically active, but allied with information from a
Figure 3-5: Illustration of the main forms of interaction of infrared radiation with a sample.
parallel study of what is detected in the gas phase, provides strong evidence of catalytic activity.

In the experimental set up used in this study, gas phase product molecules were monitored using mass spectrometry concomicantly with infrared observation of surface species. Thermal conductivity was used to monitor the gas flow before and after adsorption on the catalyst.

The physical nature of the catalyst, whether a compressed disc or a loosely held powder, can influence the kinetics of any surface reaction. For example, adsorption will occur more rapidly on a powdered sample than on a compressed disc. In a transmission infrared study, reaction tends to be diffusion controlled, and transmission infrared spectra alone may not reveal the true surface controlled kinetics of any process. Another factor affecting the dynamics of gas adsorption and reaction is the thickness of the catalyst disc. Gas may be forced round the edges or penetrate through the catalyst disc where flow is controlled by convection. In DRIFTS, there is a greater area of gas/catalyst contact.

3.5 The use of Transmission IR

3.5.1 Quantification of Transmission IR spectra

In a transmission infrared experiment, if $I_0$ is defined as the intensity of the incident beam, and $I$ the experimentally measured intensity of the transmitted beam, as illustrated in Figure 3–6, then the transmittance of the sample at a given wavenumber, $T(\bar{\nu})$ can be defined as

$$T(\bar{\nu}) = \frac{I(\bar{\nu})}{I_0(\bar{\nu})} \quad (3.1)$$

$T(\bar{\nu})$ varies with $\bar{\nu}$ resulting from absorption at particular wavelengths. For a sample of uniform optical properties and thickness, $l$, the transmit-
Figure 3–6: Illustration of incident and transmitted infrared beams.

Transmittance at an absorption band can be related to the concentration of an absorber, \( c \), by the Beer-Lambert law,

\[
T(\bar{\nu}) = \exp(-\epsilon cl)
\]  

(3.2)

where \( \epsilon \) is the molar extinction coefficient of the absorbing species defined as

\[
\epsilon = \frac{1}{cl} \ln \left[ \frac{I_0}{I} \right]
\]  

(3.3)

The transmittance, \( T(\bar{\nu}) \), is an exponential function of \( c \), and for this reason, absorbance spectra are often used instead of transmittance spectra. Absorbance, \( A(\bar{\nu}) \), and transmittance are related via

\[
A(\bar{\nu}) = -\ln[T(\bar{\nu})]
\]  

(3.4)

\[
= \epsilon cl
\]  

(3.5)

Integrated absorbance, \( \bar{A} \), is often used in infrared study of catalysts since the absorbing group may be present in a variety of bonding environments [116]. \( \bar{A} \) is defined as

\[
\bar{A} = \int_{\bar{\nu}_1}^{\bar{\nu}_2} A(\bar{\nu})d\bar{\nu}
\]  

(3.6)

\[
= \int_{\bar{\nu}_1}^{\bar{\nu}_2} \ln \left[ \frac{I_0(\bar{\nu})}{I(\bar{\nu})} \right] d\bar{\nu}
\]  

(3.7)

As in equation 3.6, \( \bar{A} \) and \( \bar{\epsilon} \), the integrated absorption coefficient, are related via
\[ A = \tilde{c}cl \] (3.8)

For a transmission infrared spectrum of adsorbed species, the total absorbance of any band at any \( \tilde{\nu} \) is the sum of absorbances due to the catalyst, \( \tilde{A}_c \), and the adsorbate, \( \tilde{A}_a \) i.e.

\[ \tilde{A} = \tilde{A}_c + \tilde{A}_a \] (3.9)

The absorbance due to the adsorbate alone is thus given by

\[ \tilde{A}_a = \tilde{A} - \tilde{A}_c \] (3.10)

\[ = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \ln \left[ \frac{I_c(\tilde{\nu})}{I(\tilde{\nu})} \right] d\tilde{\nu} \] (3.11)

\[ = \tilde{c}_a cl \] (3.12)

where \( I_c(\tilde{\nu}) \) is the intensity of the transmitted beam for the catalyst in the absence of an adsorbate, and \( \tilde{c}_a \) is the integrated absorption coefficient for the adsorbate. For a constant path length, \( l \), the concentration is directly proportional to the absorbance if \( \tilde{c} \) is constant. \( \tilde{c} \) is constant i.e. independent of sample thickness, \( l \), for vibrations of the catalyst lattice and for functional groups at the surface. However, for species adsorbed on the catalyst, \( \tilde{c} \) may vary with changing surface coverage, due to lateral interaction between adsorbed molecules.

3.5.2 Practical Application of Transmission IR

As already described, transmission infrared spectroscopy remains the most widely used form of infrared spectroscopy, for several reasons. To record a transmission infrared spectrum of an adsorbate on a catalyst surface, a self-supporting disc of catalysts must be prepared. This is generally done using a press and forming the disc under several tons of pressure. However, this is an experimentally tedious technique, and is not possible for all materials. The
sample under study must be infrared transparent in the region of interest. The thickness of disc used is generally a balance between sufficient quantity to achieve adequate sensitivity, yet not too thick such as to block out most of the infrared radiation. The disc used in this study was ~ 0.5mm thick, resulting in a loss in intensity of the infrared beam of ~ 70% on passing through the disc. Supported metal catalysts are convenient for this purpose with a low metal loading and infrared transparent support such as silica or alumina.

The disc is then placed in the path of the infrared beam at normal incidence, allowing the beam to pass through and interact with the sample and adsorbate. It is imperative that the beam can pass through the disc, for detection and analysis. The best suited materials for transmission infrared studies are those with an average particle size, \(d\), smaller than the wavelength, \(\lambda\), of the infrared radiation in the region of interest. For samples where \(\lambda \geq d\), loss of intensity occurs due to scattering by the 'large' particles. Generally, bulk absorption is too strong to allow feasible study below 1000\(\text{cm}^{-1}\), and scattering losses at high wavenumbers restrict the useful range to 4000 – 1000\(\text{cm}^{-1}\) for surface studies.

The catalyst support material also affects the transmission characteristics of the sample. For the most common support materials, SiO\(_2\) and Al\(_2\)O\(_3\), the transmission infrared range is limited at 1300 and 1100\(\text{cm}^{-1}\) respectively. This is due to strong absorption by the oxide supports below these frequencies.

In order to undertake catalytic studies on a pressed catalyst disc, the disc must be handled in an inert environment i.e. under vacuum or in an inert carrier gas. It is necessary to be able to reduce and outgas the catalyst as well as be able to pass gases over it. If realistic catalytic experiments are to be performed, the transmission infrared cell must be able to withstand reasonable gas pressures and high temperatures. Hence, a suitably designed transmission infrared cell is necessary. Another important feature is that
the infrared path length within the cell is minimised in order to reduce interference due to gas phase bands at higher gas pressures.

The cell must be equipped with infrared transmitting windows, which can be selected in conjunction with maximum gas pressure to be withstood and the infrared detector being used for the spectral region of interest. Many designs have been invoked, and a review of these was published recently [117]. The cell used in this study was specially designed, incorporating all the desirable features described above, and has been described in detail [118]. The infrared path length through the cell is 21mm. The transmission cell is shown schematically in Figures 3–7 and 3–8. The cell is made from two 77mm diameter stainless steel flanges, sealed together using a 38mm copper gasket. The cell windows were 38 x 6 mm NaCl disks (Buck Scientific), and were fitted via Viton ‘O’ Ring seal onto machined grooves on the outside of the steel flanges. These were then held on via two brass retaining plates. The catalyst was pressed into a disc incorporating a tungsten mesh, as shown in Figure 3–8, and the mesh was connected to copper heating wires spotwelded via nickel strips. The tungsten mesh was used as a localised heating element for reduction and temperature programmed desorption. The catalyst disc was then mounted between two ceramic holders and fixed onto the cell flange as shown. Gas enters and leaves the cell via stainless steel tubing connected via brass bulkhead connectors. Gas is forced through the catalyst disc, rather than across it or around the edges. A thermocouple is sprung against the edge of the disc as shown. Connections for the thermocouple and heater are via bulkhead connectors (Swagelok) within ceramic tubes, used for insulation.

The preparation of the catalyst sample for a transmission infrared study involves preparing a pressed disc of catalyst. Approximately 75 mg of catalyst was pressed into a 25 x 30 x 0.2mm tungsten wire mesh under a 10 ton pressure for 30 seconds. The pressed disc was then placed in the transmission infrared cell which was connected to the associated electrical, water and gas handling facilities. Details of these are discussed in Section 3.8.
Figure 3-7: Plan view of the transmission infrared cell.
Transmission IR Cell

Figure 3-8: Side view of the transmission infrared cell construction.
3.6 The use of DRIFTS

As described above, transmission infrared spectroscopy is not suitable for adsorption studies on catalysts where $\lambda \leq d$ or for non infrared transparent samples. A suitable technique to use in such instances is Diffuse Reflectance Spectroscopy (DRS). In a diffuse reflectance experiment, the uncompressed, powdered catalyst is placed in a sample cup with no need to prepare a pressed disc as with transmission infrared spectroscopy. In diffuse reflectance spectroscopy a scattering sample is what is required. Hence, problems which may arise from the pressing of discs can be avoided. DRIFTS has been used recently to study coals [119], pharmaceuticals [104] and catalysis [120] amongst other things. There has been a review of various applications published recently [104]. DRIFTS spectra, along with those from other new infrared techniques are more difficult to obtain than transmission infrared spectra, since the detected signal is weaker. However, with FTIR spectrometers, sufficiently good DRIFTS spectra can be obtained, and in some instances DRIFTS is the easier technique to use. Perhaps the best approach to any study is to investigate a system with both transmission infrared and with DRIFTS since each technique has certain advantages over the other. Then it can be determined which technique is most suitable for each particular system.

It has only been possible since the mid-1970s to record DRIFTS spectra with acceptable signal to noise (S/N) ratio at an adequate resolution [121]. The advent of FTIR instrumentation made it possible to detect the diffusely reflected radiation from a sample in spite of its low intensity. The available signal to noise ratio has increased enormously since the first DRIFTS spectra were recorded in 1964 using a grating instrument [122]. It is possible to detect $10^{-4} - 10^{-5}$ of a monolayer of CO adsorbed on a supported metal
catalyst [120, 123]. The potential of DRIFTS is now being realised, and in 1986, Griffiths wrote [124]

'... it will ultimately become the single most important technique for studying the chemistry of processes taking place on the surface of powdered catalysts of high surface area.'

3.6.1 Theory of DRIFTS

Diffuse reflectance describes light reflected from a matt surface. For a powdered sample, the infrared beam enters the bulk of the sample where it undergoes a variety of processes to varying degrees, including reflection, scattering, absorption, transmission, diffraction and refraction before re-emerging at the sample surface, resulting in light distributed in all directions. The diffusely reflected infrared radiation is collected by spherical or ellipsoidal mirrors and focussed onto the detector and contains some quantitative information. Specular reflection, where the angle of incidence is equal to the angle of reflection also occurs at the catalyst surface. When the specularly reflected component of the radiation is small, DRIFTS spectra are similar in appearance to transmission spectra, but are quantitatively different.

The Beer-Lambert law used in quantification of transmission infrared spectra cannot simply be applied to diffusely reflected radiation. A theory has been developed by Kubelka and Munk to describe and quantify the relationship between the light absorbed and the concentration of the absorber [125, 126]. $R_{\infty}$ is defined as the ratio of the diffuse reflectance from a sample to that of a non absorbing powder reference e.g. KBr at 'infinite depth'. This means that the sample must be placed in a cell such that an increase in its depth would cause no further change in the signal detected. In practice this means a depth of several mm [127]. A function of $R_{\infty}$, the
Kubelka-Munk function, \( f(R_{\infty}) \) is related to \( R_{\infty} \) via the equation

\[
f(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \tag{3.13}
\]

\( f(R_{\infty}) \) is related to an absorption coefficient, \( k \), and to a scattering coefficient, \( s \), via

\[
f(R_{\infty}) = \frac{k}{s} \tag{3.14}
\]

This equation is known as the Kubelka-Munk remission function. It relates the experimentally determined diffuse reflectance of an 'infinitely thick' sample to the parameters \( k \) and \( s \).

The absorption coefficient, \( k \), is related to the absorptivity, \( \alpha \), and concentration, \( c \), as

\[
k = 2.303ac \tag{3.15}
\]

and if the scattering coefficient, \( s \), is constant \( i.e. \) independent of wavelength, and the specularly reflected component of the incident infrared beam is small

\[
f(R_{\infty}) = 2.303acf = k'c \tag{3.16}
\]

Hence, \( f(R_{\infty}) \) should vary linearly with concentration, allowing the Kubelka-Munk law to be used in quantification of diffuse reflectance spectra as the Beer-Lambert law is used in transmission infrared spectroscopy. A plot of \( f(R_{\infty}) \) vs. concentration should yield a straight line passing through the origin. However, when \( \lambda \) is greater than the mean particle size, \( d \), the scattering coefficient, \( s \), becomes wavelength dependent.

The variation in absorption with concentration of adsorbate using transmission and diffuse reflectance has been compared [104]. This can be done by studying how the absorptance, \( (1-T) \), where \( T = \) transmittance varies in a transmission spectrum in the limit of low concentration of an absorber. This can be done by expanding the Beer Lambert law, and comparing with similar treatment of the Kubelka-Munk equation. For a transmission spectrum,

\[
A = -\log(T) = acl \tag{3.17}
\]
where $A$ is the absorbance, $T$ is the transmittance and $l$ is the path length through the sample. Hence,

$$T = 10^{-acl} = \exp(-2.303acl) \quad (3.18)$$

Expansion of this equation gives

$$(1 - T) = 2.303acl - 2.651a^2c^2l^2 + \ldots \quad (3.19)$$

In the limit of small $c$, the absorptance is given by $2.303acl$ and thus the signal is linearly proportional to the concentration of the absorber, $c$.

However, for diffuse reflectance, in the limit of small $c$,

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \rightarrow \frac{(1 - R_\infty)^2}{2} \quad \text{assuming } R_\infty \rightarrow 1 \quad (3.20)$$

and

$$(1 - R_\infty) = \left(\frac{4.605ac}{s}\right)^\frac{1}{2} \quad (3.21)$$

and the signal is now proportional to $\sqrt{c}$ where $c$ is the adsorbate concentration. DRIFTS is unique in having this $\sqrt{c}$ dependence, and consequently gives DRIFTS a sensitivity advantage over other techniques, at low sample concentration. Kubelka-Munk Theory was developed really for the sample diluted in a non absorbing matrix e.g. KBr, but the situation with a supported metal catalyst is somewhat different. In this study, the silica support is not wholly non absorbing, and hence is different from a non absorbing reference material. Below the cut-off the silica is wholly absorbing. The application of KM Theory to supported metal catalysts has not been wholly successful [128]. The main source of deviation from KM Theory is due to specular reflection, resulting in the linear relationship between signal and sample concentration not holding. Problems also arise with negative absorption features due to disappearance or displacement of adsorbed species.

The practical implementation of the use of KBr as a reference material would mean either diluting the catalyst with KBr, leading to fewer adsorption sites and potential sensitivity problems, and potential chemistry involving the KBr and the catalyst. The other alternative would be to record a
background spectrum of KBr and ratioing the experimental spectra against this. However, this would involve a change in the optical arrangement between recording the background and subsequent spectra. Hence, in this study absorbance plots have been used with experimental spectra ratioed against a background spectrum of the clean catalyst for all DRIFTS experiments.

3.6.2 Experimental application of DRIFTS

Several different cells have been designed for recording diffuse reflectance spectra [104, 124]. The equipment used in the DRIFTS study described here was a commercially made Spectratech ‘praying mantis’ type diffuse reflectance accessory [129]. It is compatible with commercial FTIR spectrometers, fitting into the sample compartment, and is fitted with the appropriate optics for collection of diffusely reflected infrared radiation. In practice because diffusely reflected radiation is scattered isotropically, only 10% of the diffusely reflected radiation can be collected even with the most efficient optics. Spectra with acceptable signal to noise ratio have been recorded with less than 1% throughput of radiation [130].

The DRIFTS accessory has been fitted with a controlled environmental chamber and the appropriate gas handling facilities, water cooling, a thermocouple and temperature programming facility. Detail of the position of the catalyst in the sample holder is shown in Figure 3–9. The catalyst sits in the sample cup on top of the sample post which contains a heating element. The cover fits over the sample post holding the catalyst and seats onto an ‘O’ Ring which encircles the sample post. The cover is then screwed down securely to provide a controllable environment within. The temperature of the catalyst is measured using a chromel-alumel thermocouple which enters the cell through a side arm of the cover and reaches into the catalyst sample.

The whole assembly can be raised and lowered via a sprung screw mechanism to optimise the sample position within the DRIFTS optics. The sample
Figure 3-9: Diagram of the location of the sample in the DRIFTS accessory.
holder with the cover over it is held within the DRIFTS accessory via a side arm so as not to block the infrared beam.

For a DRIFTS experiment, approximately 40 mg of catalyst was ground finely in order to reduce specular reflection, and placed in the sample holder. It was levelled off without applying pressure using the edge of a spatula. The DRIFTS cell was connected to the associated gas, water and electrical connections. Details of this and pretreatment of the catalyst are described in Section 3.8.

3.7 The use of Fourier Transform Spectroscopy

Fourier Transform (FT) spectroscopy was first developed for use in NMR spectroscopy. However, first generation computers were unable to handle the integration required in FT until the Cooley-Tukey algorithm was introduced in 1965 [131]. This made it possible to perform Fourier transformation on smaller computers and spurred the development of modern FT-NMR and FTIR spectroscopies.

In an FTIR spectrometer, the infrared beam is split into two components by a beam splitter at the centre of a Michelson Interferometer. One part of the beam is reflected via a fixed mirror, whilst the other part is reflected by a moving mirror. These then recombine at the beamsplitter to produce a beam which is then directed and focussed on to the detector. The detected signal is a variation of intensity with time, resulting from constructive and destructive interference as the moving mirror is moved.

Displacement of the moving mirror modulates the beam. A conventional intensity vs. wavelength spectrum is obtained by Fourier Transformation of the interferogram. The spectrum produced in this way is known as a single beam spectrum. A conventional transmittance or absorbance spectrum can be obtained by ratioing the single beam spectrum recorded of the catalyst
and the adsorbate against a background single beam spectrum recorded prior to adsorption.

The use of FTIR spectroscopy has several advantages over conventional dispersive spectroscopy [130, 132, 133]. Since all wavelengths are sampled simultaneously, this leads to much faster scan times. Typical scan times in FTIR spectroscopy are of the order of one second compared with many minutes in dispersive spectroscopy. This is known as Felgett’s or Multiplex advantage. This is especially important in the identification of short lived surface intermediates. Coaddition of \( n \) scans results in an improvement in the signal to noise ratio of \( \sqrt{n} \). Another advantage, known as Jacquinot’s or Throughput advantage results from the higher optical throughput of an interferometer than a grating monochromator, since there are no narrow slits involved.

The infrared source in the spectrometer used in this study is a SiC Globar rod, and the 6328 Å line of a He-Ne laser is used for accurate interferometric determination of the position of the moving mirror in the interferometer, and hence accurate determination of vibrational frequencies. Figure 3–10 shows a schematic diagram of the Michelson interferometer used in the optical bench of the spectrometer. This shows the coaxial paths of the infrared beam and the laser beam, and the separate optical paths followed by the beams after passing thorough the KBr beamsplitter at the centre of the interferometer. The infrared beam is detected using a liquid nitrogen cooled narrow band Mercury Cadmium Telluride (MCT) photoconductive detector which has a detection range of 4000 – 850 cm\(^{-1}\). The displacement of the moving mirror is shown by \( \delta \).

The infrared setup for both transmission infrared and DRIFTS studies is described below, and the experimental arrangement for gas handling and catalyst reduction is discussed in the next Section. The infrared spectrometer used for these studies as well as for the RAIRS study described in Chapter 4 was an evacuable version of the Digilab FTS-40 spectrometer [134]. It has a dedicated microcomputer for file handling, Fourier Transformation and
Figure 3–10: Schematic diagram of the interferometer used in the evacuable version of the Digilab FTS-40 spectrometer.
spectral display. The layout of the optical bench is shown in Figure 3–11. The optical bench is enclosed in an evacuable housing, and can be evacuated down to $10^{-2}$ mbar or better. This reduces or eliminates absorption bands in spectra due to atmospheric CO$_2$ and H$_2$O and prevents problems due to miscancellation of these features when spectra are ratioed. The transmission cell or the DRIFTS cell can be located in the sample compartment and the optics aligned as appropriate. Alternatively, the infrared beam can be taken out of the optical bench through evacuable housing for RAIRS studies using the associated UHV chamber. This is discussed in Chapter 4.

The optical arrangement for the transmission cell in the sample compartment is shown in Figure 3–12. For DRIFTS, the beam passes through the sample compartment, reflected within the DRIFTS accessory as shown in Figure 3–13. The infrared beam is guided using a converging mirror onto the first plane mirror in the DRIFTS accessory. From there it is directed onto the next plane mirror as illustrated and then focussed onto the sample via the first ellipsoidal mirror. The ellipsoidal mirrors can be moved apart horizontally to allow visual inspection of the beam path (the coaxial laser beam), and to achieve optimum optical alignment. The second ellipsoidal mirror captures the diffusely reflected radiation, which is then guided by the two further plane mirrors onto a series of three mirrors which focus and direct the beam through $90^\circ$ to the detector which sits on top of the spectrometer housing.

Unless otherwise stated, all spectra presented in this Chapter were recorded at $4\text{cm}^{-1}$ resolution, and are a result of 50 co-added sequential scans. Typically, it took $\sim 0.5$ s to record a single scan and so 25 seconds to record a 50 scan spectrum. Series of sequential spectra were recorded during the course of an experiment, with file handling between successive spectra requiring 30 seconds.
Figure 3-11: Schematic diagram of the layout of the optical bench.
Figure 3–12: Optical arrangement for transmission infrared experiments.
Figure 3-13: Optical path through the DRIFTS Accessory.
3.8 Experimental Setup - Mass Spectrometer / TCD Flow System

The gas handling facilities used with both the transmission and DRIFTS cells are illustrated in Figure 3-14. Particular care was taken to ensure maximum purity of the gases and adsorbates used. Otherwise, impurities in the carrier gas were a problem in producing strong absorption bands in the infrared spectra masking weaker hydrocarbon features, as well as potentially interfering with any chemistry. Helium, the carrier gas, was passed through a trap containing copper turnings heated to 523K to remove any CO, and an 'oxy' trap was used to remove any oxygen present. A silica gel trap and two liquid nitrogen traps were also used to remove any water that was present. The hydrogen was passed through two liquid nitrogen cooled zeolite molecular sieve traps to remove water.

After loading the sample cup for a DRIFTS experiment, or setting up the transmission IR cell, helium was allowed to flow over the catalyst for a short time. In both transmission and DRIFTS experiments, the catalyst was reduced at 573K under 100% flowing H₂ (100cm³/min.) for 1 hour, and then outgassed at 573K in 100% flowing He (12cm³/min.) for 30 minutes. The catalyst was then cooled to the desired reaction temperature under flowing He, and a background spectrum was recorded. The maximum temperature that could be used for the DRIFTS cell is limited by the heater rating to 573K, and although the transmission cell can be operated at higher temperature, the maximum temperature used was also 573K, to allow comparison to be made between the two techniques. Neither the DRIFTS or the transmission cell could be operated below room temperature as there was no cooling facility to either, and hence the minimum temperature that could be used was approximately ambient. Temperature programming was via a Farnell D 30/4 power supply where the current or voltage can be controlled (maximum output 4A/30V). All experiments were carried out with the apparatus
Figure 3–14: Gas handling arrangement for transmission and DRIFTS.
set up as a flow system. Following adsorption, the catalyst was heated at an approximately linear rate (~0.5K/s) in order to follow desorption using infrared spectroscopy to monitor surface species and mass spectroscopy to detect gas phase products.

Gases used for adsorption were handled using the glass vacuum line which was diffusion pumped to $10^{-6}$ mbar or better. The hydrocarbon gases were purified prior to adsorption using freeze-thaw cycles. Gases were adsorbed on the catalyst via pulses of a measured pressure in an enclosed volume (sample loop) injected into the helium carrier gas stream. The uptake of gas by the catalyst was monitored by a thermal conductivity detector (TCD), analysing the gas before and after passing over the catalyst. A sample of the product gas stream was drawn off via the jet separator to be sampled by the mass spectrometer to allow identification of gas phase products.

3.9 DRIFTS and Transmission Spectra

An example of a typical interferogram is shown in Figure 3–15. A single beam spectrum computed from the recorded interferogram in the absence of either the DRIFTS or transmission cell i.e. straight through the spectrometer, is shown in Figure 3–16. The detected signal is composed of characteristics of the IR source, the detector and associated optics and shows maximum response at 1300cm$^{-1}$. Examples of single beam spectra computed from the appropriate interferograms recorded for transmission and DRIFTS operation are shown in Figure 3–17. The integrated intensity of the transmission single beam spectrum is considerably more than that of the DRIFTS single beam spectrum. The same single beam spectra are shown normalised in Figure 3–18. As already mentioned, the signal giving rise to each single beam spectrum is composed from several interaction processes of the infrared radiation with the sample. The DRIFTS single beam spectrum consists of diffusely reflected radiation and specular reflection from the cat-
Figure 3-15: Example of an interferogram.

allyst surface. Specular reflection is observable below the 1350 cm\(^{-1}\) cut-off. This carries no relevant information in a DRIFTS study.

The transmission IR single beam spectrum is composed of transmitted and diffusely transmitted radiation, and radiation is also scattered by the catalyst although it is not generally detected. The poorer signal intensity at higher wavenumbers in transmission is due to scattering by catalyst particles which is most severe at high wavenumber. Above 2200 cm\(^{-1}\), DRIFTS has higher sensitivity than transmission for a scattering sample.

The overall poorer detector response in DRIFTS is partly offset against that in transmission by the higher equivalent path length through the sample [118]. For EuroPt-1, the silica support material is essentially transparent in this region (high \(\tilde{\nu}\)), hence adsorbate vibrations observed using DRIFTS will be enhanced relative to those detected using transmission. Below 2200 cm\(^{-1}\) the silica is strongly absorbing and the opposite situation occurs and transmission has higher sensitivity over DRIFTS. The quite dis-
Figure 3-16: Single beam spectrum in the absence of the DRIFTS or transmission cell.
Figure 3-17: Single beam spectra recorded in (a) Transmission and (b) DRIFTS.

Figure 3-18: Normalised single beam spectra from (a) Transmission and (b) DRIFTS.
distinct peaks observed in the 1300 – 2200cm\(^{-1}\) region are due to overtone and combination bands of the silica lattice vibrations. In Figure 3–17, spectrum (a) shows a typical transmission single beam spectrum and (b) shows a single beam spectrum for DRIFTS operation. The low frequency cut-offs for EuroPt-1 are 1400cm\(^{-1}\) for DRIFTS and 1300cm\(^{-1}\) for transmission.

As already mentioned, each single beam spectrum was ratioed against the relevant background spectrum to obtain a transmittance or absorbance spectrum. An example of each kind of spectrum in the C-H stretching region 3150 \(\rightarrow\) 2750cm\(^{-1}\), computed from the same DRIFTS single beam and background spectra, is shown in Figure 3–19 for cyclopentene adsorption on EuroPt-1, recorded using DRIFTS. These spectra have been baseline corrected. The % transmittance values are negative due to baseline correction from a spectrum where the baseline was initially below 100% transmittance. All DRIFTS, transmission (and RAIRS) spectra presented in this Thesis are plotted in absorbance units as standard. The background spectrum used for the absorbance plots was recorded immediately prior to adsorption, with no changes made to the optical arrangement between recording the background and subsequent spectra.

### 3.10 Previous Work

Previous study of cyclopentene adsorption on single crystals has mainly been concerned with adsorption on Pt(111). Most of this work has been done by Avery using Electron Energy Loss Spectroscopy (EELS) and Thermal Desorption Spectroscopy (TDS) [135, 136], and by Campbell using TDS [137, 138]. To date, no studies using infrared spectroscopy to investigate adsorption of these molecules on supported metal catalysts have been reported. Avery has also investigated cyclopentane adsorption on Pt(111) [139], but there are no reported vibrational studies of methylcyclopentane adsorption on single crystals. There have been kinetic studies of methylcyclopentane
Figure 3-19: (a) Transmittance and (b) absorbance DRIFTS spectra for cyclopentene adsorbed on EuroPt-1 (3150 → 2750 cm⁻¹).
Cyclopentene has been observed using EELS to adsorb molecularly on Pt(111) at 90/100K in an \( \eta^2 \)-\( (\text{di-}\sigma) \)-configuration bonded through the alkene carbon atoms. Monolayer coverage is achieved at \( \theta = 0.24 \) [137]. On heating, cyclopentene partially desorbs molecularly (280–300K), and partially dehydrogenates to produce adsorbed hydrogen and a stable parallel bonded \( \eta^5 \)-cyclopentadienyl species (C\(_5\)H\(_5\)) in the temperature range 250 – 300K. This is similar to inorganic metallocenes such as ferrocene, Fe(C\(_5\)H\(_5\))\(_2\). Further heating results in dehydrogenation of the cyclopentadienyl species, liberating gaseous hydrogen. From 402 – 575K, it is converted to adsorbed specie
/ species with a stoichiometry $C_5H_2$. Raising the temperature further still, from 500–800K results in further dissociation producing adsorbed hydrogen atoms which immediately desorb molecularly leaving graphitic carbon on the surface.

The extent to which each of dehydrogenation and molecular desorption occur has been found to depend on the surface coverage of cyclopentene [137]. At low coverage, approximately 98% dehydrogenates during TDS whereas at near monolayer coverage around 60% dehydrogenates. Avery has proposed that molecular desorption of cyclopentene results from steric displacement by the larger $\eta_5$-cyclopentadienyl species.

The behaviour of cyclopentene upon adsorption can be contrasted with that of the linear alkene ethene. At low temperature, a similar di-σ bonded ethene species is formed [143]. Between 250 – 300K, the di-σ bonded ethene partially dehydrogenates to ethylidyne, $\equiv C-CH_3$ [143-145]. The adsorbed ethylidyne is stable on Pt(111) to around 500K, and above this temperature dehydrogenation leads to graphite formation on the surface. As described above, C-C bond rupture was not observed for cyclopentene, preventing formation of an alkylidyne species as observed with ethene.

The only vibrational data for cyclopentene adsorption on platinum has been the EELS studies reported by Avery [135, 136]. EELS was used to spectroscopically identify the adsorbed cyclopentene and cyclopentadienyl species. The EELS spectra recorded after heating a cyclopentene saturated Pt(111) surface to 200K and 370K are reproduced in Figure 3–21.

At 200K, peaks were observed due to adsorbed cyclopentene in the CH stretching region at 2970, 2890 and 2750cm$^{-1}$, as well as many bands in the CH deformation region. On heating the crystal to higher temperature, the much simplified spectrum showing a band in the CH stretching region at 3070cm$^{-1}$ and a band at 840cm$^{-1}$, indicative of higher symmetry was observed. Exchange experiments with a D$_2$ molecular beam have confirmed that the bands above 3000cm$^{-1}$ and at 840cm$^{-1}$ were due to vibrations involving hydrogen atoms, providing evidence that this spectrum was due to
Figure 3–21: EELS spectra from cyclopentene adsorbed on Pt(111), from [135] (a) after heating a saturated surface to 200K and (b) of the cyclopentadienyl species after heating to 370K.

the η₅-C₅H₅ species. The EELS spectrum is stable to 480K and then the η₅-C₅H₅ species undergoes further dehydrogenation with the average composition of the residual species (CH)ₙ.

A low frequency ν (CH) peak observed at 2695cm⁻¹ at low coverage which shifts to 2750cm⁻¹ at saturation coverage has been attributed to the CH stretching vibrations 'softened' by hydrogen bonding to the surface [146]. Such softened modes have been observed spectroscopically for several adsorption systems. Softening has been seen in EELS spectra of ethene on Ni(111) [146], and cyclohexane on Pt(111) [146], Ni(111) [146], Ni[5(111)×(110)][11], and for C₅ and C₆ hydrocarbons on Ru(001) [147]. The softened ν CH mode of cyclohexane has been observed on a variety of surfaces using EELS [148], including Ni(110) [148], Pd(111) [149], Pd(110)
[150], Cu(100) [35] and Cu(111) [35]. Such broad shifted soft bands have also been observed using RAIRS, although it is more difficult to record using RAIRS than with EELS as the low intensity and broadness of the feature can be difficult to discriminate from the background [151]. Softening has been observed using RAIRS for cyclohexane on Pt(111) [151] and Pt(100) [152], and more weakly for cyclopentane, hexane and 2,2-dimethylpropane [151].

There have been two reported EELS studies of cyclopentane adsorption using vibrational spectroscopy on single crystal surfaces, on Pt(111) [139] and Ru(001) [153], and a RAIRS spectrum of cyclopentane on Pt(111) has been published [151]. The EELS spectra for cyclopentane on Pt(111) showed evidence of multilayer adsorption at 90K with a peak in the $\nu$ (CH) region at 2960cm$^{-1}$. On heating to 180K a new peak was also observed, at 2690cm$^{-1}$, attributed to a soft C-H stretch resulting from weakening of the cyclopentane $\textit{via}$ hydrogen bonding to the Pt surface. The spectrum observed at that point is consistent with the cyclopentane molecule being hydrogen bonded to the surface with the ring being approximately parallel to the surface. Further heating led to two bands in the $\nu$ (CH) region at 2670 and 2970cm$^{-1}$, giving an EELS spectrum characteristic of $\eta_2$-di-$\sigma$ cyclopentene. Heating to 260K resulted in weak features observed at 2990 and 3060cm$^{-1}$, as well as a strong band at 840cm$^{-1}$ and another band at 350cm$^{-1}$, due to dehydrogenation to an $\eta_5$-cyclopentadienyl species, as was observed for cyclopentene adsorption after heating on Pt(111). The RAIRS spectrum of cyclopentane on Pt(111) showed evidence of a soft band, although not as strong as that seen for cyclohexane on Pt(111) [151].

On Ru(001), cyclopentane was adsorbed as a monolayer at 170K, with bands observed in the CH stretching region at 2935cm$^{-1}$, and a soft band at 2610cm$^{-1}$ as well as bands at lower wavenumber. Heating to 200K results in formation of adsorbed cyclopentene with CH stretching vibrations observed at 2855 and 3057cm$^{-1}$.
3.11 Results

The results presented below are from experiments involving adsorption of three small cyclic hydrocarbon molecules (cyclopentene, cyclopentane and methylcyclopentane) on EuroPt-1. EuroPt-1 is a standard Pt/SiO₂ catalyst prepared for the Council of Europe, which has been well characterised and studied by many groups using many techniques [154-158]. A detailed review of all recent work on EuroPt-1 has been published [159]. The main properties of EuroPt-1 are summarised in Appendix B. Experiments were also carried out using silica as the adsorbent, reduced and outgassed in exactly the same manner as the EuroPt-1 samples. The silica used was similar to that used in the preparation of EuroPt-1 (Sorbosil grade AQ U30 silica gel, Crosfield Chemicals).

For each experiment, a series of sequential spectra was recorded during adsorption from a series of pulses of hydrocarbon injected into 100% flowing helium. Unless otherwise stated, each pulse contained 0.14 μmoles of hydrocarbon from a 0.02 bar pressure of gas in the sample loop. As already described, the ingoing and outcoming pulses were followed using a thermal conductivity detector (TCD). The trace from the TCD was used to correlate the pulses with the infrared spectra recorded, and to derive quantitative information on the uptake of hydrocarbon by the catalyst. Gas phase products were monitored using a mass spectrometer to analyse a small amount of the exit gas stream drawn off through the jet separator. The mass spectrometer was set to scan the relevant mass range during the course of an experiment.

The spectra recorded during an experiment were ratioed against a 250 scan background spectrum recorded immediately prior to adsorption. All series of spectra and associated graphs referred to below are grouped together at the end of this Chapter for ease of reference. All spectra have been baseline corrected over the region plotted. This is particularly necessary for spectra recorded at high temperatures since the ratioed spectra curve
sharply in the region of interest and small absorption bands are otherwise difficult to observe.

3.11.1 Cyclopentene

DRIFTS Studies

Figures 3–30 and 3–31 show a series of spectra recorded using DRIFTS during adsorption on EuroPt-1 from five sequential pulses of cyclopentene. The region shown is the CH stretching region $\nu$ (CH) (3150 $\rightarrow$ 2750cm$^{-1}$). Each spectrum was recorded over a 25s time interval, and the time interval between successive spectra is 30s. The ingoing and outcoming pulses are shown on the right of the spectra on the same timescale, although not to quantitative scale, to illustrate their temporal relationship to the recorded spectra. The narrow TCD peak, peaking to the left corresponds to the ingoing hydrocarbon pulse, and the broader TCD peak to the right is that detected after passing over the catalyst, and these are further discussed below. On adsorption of cyclopentene at 310K, IR bands are observed at 3059, 2955, 2850 and 2801cm$^{-1}$. The average position of each band is quoted in all cases. Some variation in frequency of some of the peaks was observed, and this will be discussed later. All band frequencies are labelled on the spectra.

The uptake of the cyclopentene by the catalyst was calculated using the integrated intensities of the ingoing and outcoming TCD peaks. For the five pulses, an uptake of 63%, 63%, 47%, 51% and 26% of the ingoing pulse was taken up by the catalyst, for pulses 1–5 respectively. This corresponds to a total uptake of cyclopentene by the catalyst of 0.35 $\mu$moles or 8.8 $\mu$mol g$^{-1}$ catalyst.

No peaks were observed in the CH deformation region $\delta$ (CH) (1550 $\rightarrow$ 1080cm$^{-1}$) due to the poor sensitivity of DRIFTS for silica supported materials in this region [56], and hence all spectra presented here are of the CH stretching region. The intensity of each band is plotted in absorbance units
as a function of time in Figure 3–32. Time = zero was taken for this, and subsequent similar graphs to be when the hydrocarbon pulse reached the catalyst. Each symbol in the graph represents the intensity of the relevant band in the successive infrared spectra in the series. The first intensity points plotted in Figure 3–32 correspond to the third spectrum shown in the series in Figure 3–30. The two preceding spectra shown in Figure 3–30 are included to show the relationship of the recorded spectra to the ingoing and outcoming TCD peaks. This graph shows a general increase in intensity of all bands during adsorption. The 2850cm\(^{-1}\) band was always the most intense band, and its behaviour immediately following a pulse of cyclopentene was to show a considerable increase in intensity, followed by a slight loss in intensity, and showing smaller incremental increases following successive pulses, particularly the later pulses. This agrees with the TCD observation of decreasing uptake from the later pulses, particularly pulse 5. The 2955cm\(^{-1}\) band shows a similar increase following each pulse, with a more marked decrease in intensity than for the 2850cm\(^{-1}\) band following this. It is not a symmetrical peak, perhaps having contributions from underlying shoulders or small peaks and may contain some contribution from the gas phase or a weakly held (physisorbed) surface species. The two bands at 3059 and 2807cm\(^{-1}\) are weaker, and although reflecting the behaviour of the other bands, tend to saturation after \(\sim 500\)s (3 pulses).

The composition of the gas phase was monitored continuously across the mass/charge \((m/z) = 60 \rightarrow 70\) region of the mass spectrum. For the DRIFTS study of cyclopentene adsorption on EuroPt-1, the temporal relationship between the TCD trace, the mass spectral 67 peak intensity, IR spectra and time is shown for the first cyclopentene pulse in Figure 3–22. Cyclopentene has its major peak in the mass spectrum at \((m/z) = 67\). Figure 3–22 shows the ingoing (narrow) and outcoming (broad) pulses of cyclopentene in the TCD trace, and the delay (32s) in mass spectral observation of the pulse due to the relative physical positions of the TCD, DRIFTS cell and the mass spectrometer. The delay in the mass spectral observation of the pulse is dependent
on the flow rate of the carrier gas, and hence the flow rate was kept constant throughout this series of experiments. In mass spectral determination of the peak maxima, this delay was taken into account. The ingoing pulse gives rise to a narrow TCD peak, whereas the outcoming pulse is much broader after passage through the catalyst with adsorption and diffusion leading to the broadening of the outcoming peak. The ingoing and outcoming TCD peaks peak in opposite directions as the gas flow is in opposite directions through the thermal conductivity detector where the difference in thermal conductivity relative to the carrier gas (helium) is measured.

In the DRIFTS experiment, the m/z = 67 peak increased in intensity as illustrated in Figure 3–22 following each pulse. During the fourth and fifth pulses, as the m/z = 67 peak was diminishing after passing through maximum intensity, the m/z = 70 peak increased slightly indicating the formation of cyclopentane, which has a fragment in its cracking pattern at m/z = 70 (relative intensity 29%), although its major peak is at m/z = 42 (relative
intensity 100%). The temporal relationship between the m/z = 67 and 70 peaks for the fifth pulse is shown in Figure 3–23, showing the m/z = 70 peak increasing in intensity after the m/z = 67 peak has passed through a maximum and is decreasing in intensity. The m/z = 70 peak may arise from hydrogenation of cyclopentene to cyclopentane from residual hydrogen on the catalyst surface or within the mass spectrometer (the cyclopentene contains 1% cyclopentane impurity). The normalised integrated areas under the m/z = 67 peak following each pulse during adsorption are 0.56, 0.75, 0.78, 0.88 and 0.87 for peaks 1–5 respectively. This indicates increasing amounts of gas phase cyclopentene and thus decreasing uptake by the catalyst.

Figure 3–23: Illustration of m/z = 67 and 70 peak intensities following the fifth pulse of cyclopentene.

A series of spectra was recorded during temperature programming of the catalyst to 573K, at a heating rate of ~0.5K/s, following the adsorption of cyclopentene, and is shown in Figure 3–33. The average temperature of the

"These integrated areas are normalised. Similarly for cyclopentene / EuroPt-1 (transmission) and cyclopentene / silica (DRIFTS), all peaks are normalised to 1 for the peak following the third pulse in the cyclopentene / silica experiment."
catalyst as a spectrum was recorded is marked at the side of each spectrum. The last two spectra of the series are also plotted separately in Figure 3-34 where the bands can be seen more clearly. The intensity of bands observed during adsorption decreases as the catalyst temperature is increased, and at around 388K, the band at 2955cm\(^{-1}\) decays and a peak grows at 2969cm\(^{-1}\) with two small peaks emerging at 2932 and 2909cm\(^{-1}\). The 2969cm\(^{-1}\) peak seems to have contributed to the asymmetry of the 2955cm\(^{-1}\) band. The intensity of the bands observed during temperature programmed desorption is plotted as a function of temperature in Figure 3-35.

This graph shows a steep decrease in intensity of the 2850cm\(^{-1}\) band, and a corresponding decline in the 2955cm\(^{-1}\) peak intensity. The bands at 3059 and 2801cm\(^{-1}\) decay gradually and the new peaks observed at 2932 and 2909cm\(^{-1}\) emerge above 388K and after passing through maximum intensities at 498K, then decrease in intensity.

During TPD, there was a small increase in the m/z = 70 peak with a maximum intensity at 358K. There was no mass spectral evidence of gas phase products at higher temperature. The TCD trace showed some evidence of desorption with very weak maxima observed at approximately 348 and 548K.

The species responsible for the new emerging peaks at 2932 and 2909cm\(^{-1}\) were investigated in another experiment following cyclopentene adsorption by pulsing with hydrogen at both the adsorption temperature and also after heating to 483K. These peaks were not observed in TPD of cyclopentene from silica, confirming that they are due to species adsorbed on the metal.

Two DRIFTS experiments are described below, investigating surface reaction of cyclopentene with hydrogen. Cyclopentene was adsorbed on EuroPt-1 as before, and then pulses of hydrogen were injected into the helium gas flow to investigate its effect on surface species. Both experiments described here involved the adsorption from 0.05 bar cyclopentene pulses, thus containing 0.36 µmoles, and each infrared spectrum was collected using 100 sequential scans, doubling the acquisition time of the previous 50
scan spectra. This was necessary to achieve sufficient sensitivity with the infrared spectrometer due to poorer performance during these experiments. The spectra were recorded at the same resolution of 4 cm\(^{-1}\) as before.

In the first experiment, cyclopentene was pulsed onto the catalyst at 310K as before. Similar bands were observed in the DRIFTS spectrum, at 3057, 2954, 2851 and 2801 cm\(^{-1}\). Following adsorption from three successive cyclopentene pulses, 2 \(\mu\)mole pulses of hydrogen were injected into the helium low, and pulsed onto the catalyst, which was held at 310K. The series of spectra recorded during admission of the hydrogen pulses is shown as a function of spectrum number in Figure 3–36, and the spectra are numbered for reference. The TCD trace beside the series of spectra shows the narrow ingoing hydrogen pulse, and the broader outcoming pulse. The ingoing hydrogen pulse shows deflection in the opposite direction to that observed for hydrocarbons, since the thermal conductivity is measured relative to helium. The corresponding plot of band intensities from this series of spectra is shown in Figure 3–37. The effect of the first pulse of hydrogen was to shift both the 2851 and the 2954 cm\(^{-1}\) bands to 2857 and 2963 cm\(^{-1}\) respectively. The 2963 cm\(^{-1}\) peak showed a large increase in intensity in the infrared spectrum immediately following the first hydrogen pulse, whereas the 2857 cm\(^{-1}\) peak showed a concomitant decrease in intensity from the immediately preceding spectrum. The 3057 cm\(^{-1}\) peak dropped to zero intensity immediately following the hydrogen pulse and the 2801 cm\(^{-1}\) peak gradually lost intensity throughout the following series of spectra. A further two pulses of hydrogen gave rise to small increases in the intensity of the 2945 cm\(^{-1}\) peak immediately following a pulse, and then a gradual decrease in intensity.

The mass spectrum was scanned to monitor the \(m/z = 67\) peak during cyclopentene adsorption, and showed similar behaviour to the initial cyclopentene adsorption experiment described earlier. During hydrogen pulsing, the \(m/z = 67\) peak was of constant background intensity, and the \(m/z = 70\) peak was observed to grow in intensity following each pulse. The \(m/z = 42\) peak
was then followed and passed through a maximum following the next two hydrogen pulses. The TCD trace during hydrogen pulsing showed peaks of decreasing intensities following each hydrogen pulse, indicating a maximum gas phase quantity following the first hydrogen pulse, and decreasing amounts following the next two hydrogen pulses.

The other hydrogen pulsing experiment described here involved adsorption of cyclopentene on EuroPt-1 at 310K from three 0.36 μmole cyclopentene pulses, and then the catalyst was heated to 483K before pulsing with 2 μmole pulses of hydrogen. The series of DRIFTS spectra recorded during heating to 483K following adsorption is shown in Figure 3-38, with temperatures marked at the side of each spectrum. These spectra show similar behaviour to those in the previously described cyclopentene adsorption experiment. Bands were initially observed at 3057, 2955, 2851 and 2800 cm\(^{-1}\). During heating, the 2955 cm\(^{-1}\) band decayed in intensity, shifting to 2967 cm\(^{-1}\). The two small peaks previously observed on heating adsorbed cyclopentene emerged at 2930 and 2909 cm\(^{-1}\) above 393K. When the first hydrogen pulse arrived at the catalyst, the 2930 cm\(^{-1}\) band was observed to shift to 2934 cm\(^{-1}\), and the 3057 cm\(^{-1}\) band which had shifted to 3063 cm\(^{-1}\) lost most of its intensity. DRIFTS spectra are shown as far as was possible to baseline correct, due to the steeply curving baseline and low concentration of surface species at higher temperatures. The TCD trace showed a more intense outcoming pulse following the first pulse of hydrogen than following the second. Following the two pulses of hydrogen at 483K, the catalyst was heated to 573K, but there was no TCD evidence of any gas phase species being produced. No useful information was obtained from the mass spectral trace, probably due to the low concentration of material at this stage.

The adsorption of cyclopentene on silica was also studied using DRIFTS. Spectra recorded during adsorption are shown in Figure 3-39. Bands were observed at 2957 and 2867 cm\(^{-1}\), with a shoulder at 2923 cm\(^{-1}\). There is a hint of a band at 3053 cm\(^{-1}\) following each pulse which rapidly vanishes. The intensities of the two main bands are shown as a function of time dur-
ing adsorption in Figure 3–40. As for cyclopentene on EuroPt-1 described earlier, the plot of band intensities was started from the third spectrum shown in Figure 3–39 with each symbol representing the intensity of a peak in subsequent spectra. Generally, the intensity of the bands observed on silica are much weaker than the those observed on EuroPt-1, reflected by the lower absolute signal and consequently lower signal to noise ratio in the series of spectra in Figure 3–39. The two main bands show a large increase in intensity following each pulse, followed by a significant drop in intensity (ranging from 25–40%). The integrated TCD peaks observed during adsorption of cyclopentene on silica showed an uptake of 38%, 39% and 51% following the three pulses corresponding to a total uptake of 0.6 μmoles, or 15 μmol g⁻¹ silica. The mass spectra showed an increase in both the m/z = 67 and 70 peak intensities following the pulses of cyclopentene. The normalised integrated areas under the m/z = 67 peak were 0.72, 0.95 and 1.00 following pulses 1–3 respectively.

Spectra recorded during TPD at a heating rate of ~0.6K/s are shown in Figure 3–41. The intensities of the two bands are shown as a function of temperature during TPD in Figure 3–42. Both the 2957 and 2867cm⁻¹ bands decay to zero intensity by 393K, with a maximum rate of decay at 368K. The TCD trace showed a maximum at 353K. During the TPD, there was a small increase in the m/z = 67 and 70 peaks, with maxima at 348K.

**Transmission IR Studies**

Cyclopentene adsorption on EuroPt-1 was also investigated using transmission IR, in order to compare results from similar experiments using DRIFTS and transmission infrared spectroscopy. No CH deformation bands were observed in the transmission experiments. A series of transmission IR spectra recorded during adsorption from three 0.14 μmole cyclopentene pulses is shown in Figure 3–43, with the band intensities plotted as a function of time during adsorption in Figure 3–44. As before, the first set of intensity data was taken for the spectrum recorded immediately prior to the appear-
The frequencies of the bands observed using transmission infrared spectroscopy are slightly different to those observed using DRIFTS. Band intensities increase much more slowly than in DRIFTS, with bands generally less distinct in transmission. Noticeably, the signal to noise ratio in the transmission spectra is considerably higher than for the equivalent DRIFTS spectra.

Mass spectral analysis of the gas phase during the transmission infrared experiment again showed an increase in the m/z = 67 peak intensity following each pulse, although the mass spectral peak intensities were very much weaker than in the corresponding DRIFTS experiment, reflected by the normalised m/z = 67 peak integrals following pulses 1–3 of 0.15, 0.26 and 0.50. This arises from the higher quantity of catalyst used to make the
transmission disc, although the amount of catalyst in the infrared beam path is similar for both the DRIFTS and transmission samples.

The series of spectra recorded using transmission infrared spectroscopy during TPD of cyclopentene from EuroPt-1 is shown in Figure 3–45. The final spectrum is shown more clearly in Figure 3–46 for comparison with the equivalent DRIFTS spectra. The heating rate used in this experiment was ∼0.5K/s. Band intensities are shown as a function of temperature in Figure 3–47. The 2962cm⁻¹ band drops steadily in intensity with increasing temperature. The 2852cm⁻¹ band decreases in intensity, and the 3062cm⁻¹ band remains quite steady in intensity until above 483K. The 2806cm⁻¹ band decreases to very low intensity by 403K, and all bands have decayed to zero intensity by 513K. During TPD the decay of peaks is less marked than observed using DRIFTS. The 2932 and 2909cm⁻¹ bands observed using DRIFTS are not apparent as distinct peaks, although shoulders to the 3062 and 2962cm⁻¹ bands emerge at higher temperature in the series of transmission spectra, at 3037, 2982 and 2931cm⁻¹. The decay in intensity of the 2962cm⁻¹ peak could not be accurately curvefitted. No change in the mass spectral peak intensities in the m/z = 65–75 region was observed. The TCD trace showed a desorption maximum at 373–383K, and a small amount of steady desorption with increasing temperature.

3.11.2 Cyclopentane

Spectra recorded using DRIFTS during adsorption of cyclopentane on EuroPt-1 at 309K are shown in Figure 3–48, from 3050 → 2750cm⁻¹. A plot of band intensities during adsorption is shown in Figure 3–49, starting with intensity measurements from the spectrum immediately prior to the appearance of absorption bands. Peaks were observed at 2949, 2859 and 2804cm⁻¹. During adsorption, the broad 2949cm⁻¹ peak intensity increases dramatically immediately following a pulse of cyclopentane, reflected in the large peaks, but then decay rapidly following the increase, illustrated clearly in Figure
The 2859 cm\(^{-1}\) peak shows a large increase in intensity following the first pulse, and then a steady increase in intensity. Noticeably, the intensity of the 2859 cm\(^{-1}\) band does not drop off following a pulse as was observed with cyclopentene, but in fact remains steady or increases. The decay of the 2949 cm\(^{-1}\) peak may contribute to the steady/increasing 2859 cm\(^{-1}\) peak. The 2804 cm\(^{-1}\) peak is much always weaker and shows a steady increase in intensity with time. The uptake from the three pulses could not be quantified accurately from the TCD trace in this experiment.

Spectra recorded during subsequent TPD are shown in Figure 3–50. Band intensities during TPD are plotted as a function of temperature in Figure 3–51. The heating rate in this experiment was \(\approx 0.5 \text{K/s}\). Desorption is straightforward and complete by 428K, with no IR evidence of any surface species remaining beyond this temperature.

Adsorption of cyclopentane on silica was also studied using DRIFTS. Spectra recorded during adsorption are shown in Figure 3–52. The behaviour of band intensities during adsorption is shown in Figure 3–53. A broad envelope is apparent with main peaks at 2957 and 2870 cm\(^{-1}\) and a shoulder at 2920 cm\(^{-1}\). Both the 2957 and 2870 cm\(^{-1}\) bands show a similar behaviour, increasing considerably in intensity immediately following each pulse, and then dropping back in intensity. The intensity drops back to almost what the intensity was prior to the pulse for both the second and third pulses, indicating removal of gas phase or weakly held species in the flowing helium. The uptake determined from the TCD trace was 29%, 26% and 31% for the three pulses, corresponding to a total uptake of 0.12 \(\mu\)moles or 3 \(\mu\)mol g\(^{-1}\) silica.

The series of spectra recorded during TPD at \(\sim 0.5 \text{K/s}\) is shown in Figure 3–54. Desorption of cyclopentane occurs by 373K, with a steady decrease in the intensity of both main peaks. The behaviour of peak heights with temperature during TPD is plotted in Figure 3–55. The TCD trace showed a maximum at 353K.
3.11.3 Methylcyclopentane

The adsorption of methylcyclopentane on EuroPt-1 was also investigated using DRIFTS. The spectra shown in Figure 3–56 (3050 → 2750 cm⁻¹) were recorded during adsorption at 309K. An envelope of peaks was observed, with maxima at 2946, 2907, 2855 and 2808 cm⁻¹. The behaviour of peak intensities during adsorption is shown as a function of time in Figure 3–57. The 2808 cm⁻¹ peak intensity increased steadily but the 2855 and 2907 cm⁻¹ peaks showed a slight rise after the first pulse and remained steady following subsequent pulses. Initially, the 2946 cm⁻¹ peak was the most intense but in the time between the first and second pulses it drops in intensity and the 2855 cm⁻¹ peak becomes the most intense. The 2946 cm⁻¹ peak shows similar behaviour following subsequent pulses indicating a substantial contribution from gas phase or a weakly held species which is swept away in the gas flow. The 2946 cm⁻¹ peak showed a dramatic intensity increase following each pulse and then a considerable loss in intensity. This behaviour is similar to that observed for cyclopentane on Europt-1 where the 2859 cm⁻¹ peak did not show the large decreases in intensity observed for cyclopentene. The loss in intensity of the 2949 cm⁻¹ peak may again contribute to maintaining the intensity of the 2907 and 2853 cm⁻¹ peaks. The uptake from the three pulses determined from the TCD trace is 47%, 21% and 8%, giving a total uptake from the three pulses of 0.11 µmoles or 2.8 µmol g⁻¹ catalyst.

The series of spectra recorded using DRIFTS during TPD of methylcyclopentane from EuroPt-1 is shown in Figure 3–58. During TPD, at ~0.7 K/s, all peaks decay steadily in intensity to zero by about 453K. At 363 and 393K the 2907 cm⁻¹ peak shows two resolved maxima at 2904 and 2895 cm⁻¹, with the 2895 cm⁻¹ peak dominating the 393K spectrum. Peak intensities are plotted as a function of temperature in Figure 3–59. A maximum was observed in the TCD trace at 343–348K.

A corresponding study of the adsorption of methylcyclopentane on silica using DRIFTS reveals two main peaks at 2954 and 2869 cm⁻¹ and a shoulder.
at 2912 cm\(^{-1}\), as shown in Figure 3–60. The intensities of these bands are plotted as a function of time during adsorption in Figure 3–61. Both show considerable increase in intensity following each pulse followed by a loss in intensity. The uptake from the three pulses determined from the TCD trace was 32%, 30% and 37%, corresponding to a total uptake of 0.14 \(\mu\)moles, or 3.5\(\mu\)mol g\(^{-1}\) silica.

Spectra recorded during subsequent TPD are shown in Figure 3–62, and show no evidence of surface species remaining above 383K. Plots of the absorbance of each main band during TPD are shown in Figure 3–63. This shows a steady decrease in intensity of both bands to zero at 383K. The TCD trace shows a maximum in the gas phase at 353K.

3.12 Discussion

3.12.1 Cyclopentene

The spectra recorded for cyclopentene adsorbed on EuroPt-1 show several intense peaks in the CH stretching region, at 3059, 2955, 2850 and 2801 cm\(^{-1}\). Of the three molecules studied, cyclopentene showed the strongest absorption bands. The band frequencies observed for cyclopentene adsorbed on EuroPt-1 and silica recorded using DRIFTS, and on EuroPt-1 recorded using transmission infrared spectroscopy are listed with their relative intensities in Table 3–3, along with the proposed assignment of the bands.

The assignment of the bands was made on the basis of the appropriate literature IR and Raman spectra, and spectra from other surface studies which are listed in Tables 3–4 and 3–5, together with the relevant symmetry species for gas phase cyclopentene under \(C_{2v}\) symmetry. The bands observed in the DRIFTS spectra will consist of several contributions. These may include gas phase cyclopentene vibrations, as listed in Table 3–4, and weakly held (physisorbed) cyclopentene on both the metal and the support,
Table 3-3: Position of IR bands observed for cyclopentene.

<table>
<thead>
<tr>
<th>Proposed Assignment</th>
<th>DRIFTS EuroPt-1</th>
<th>DRIFTS silica</th>
<th>Transmission EuroPt-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu \ (\text{CH})_{\text{sym}}$ A$_1$</td>
<td>3059(w)$^a$</td>
<td>3062(w)</td>
<td></td>
</tr>
<tr>
<td>$\nu \ (\text{CH})_{\text{asym}}$ B$_2$</td>
<td>2955(m)</td>
<td>2957(s)</td>
<td>2962(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2923(sh)</td>
</tr>
<tr>
<td>$\nu \ (\text{CH$<em>2$})</em>{\text{sym}}$ A$_1$</td>
<td>2850(s)</td>
<td>2867(m)</td>
<td>2852(m)</td>
</tr>
<tr>
<td>$2\delta \ (\text{CH$_2$})$</td>
<td>2801(w)</td>
<td></td>
<td>2806(w)</td>
</tr>
</tbody>
</table>

$^a$ (s), (m), (w) indicate the relative strengths of the bands

$^b$ In this and later Tables (s) = strong, (m) = medium, (w) = weak (sh) = shoulder

as well as more strongly held (chemisorbed) species. Linewidth and intensity changes, whether enhancement or attenuation due to the MSSR may help to distinguish these different forms of cyclopentene. More strongly held (chemisorbed) species will be retained on the surface in the flow system while weakly held species may be swept away. The strength of adsorption of the various species on both the metal and on silica can be estimated using TPD. Bands due to cyclopentene on the metal and on the silica can be distinguished from intensity changes in the presence of the metal, and from a comparison of spectra from EuroPt-1 and silica.

Intuitively, bonding of cyclopentene as a flat planar molecule on the metal surface would be anticipated, and this is corroborated by Avery’s EELS results. The gas phase spectrum discussed earlier [160] was interpreted in terms of $C_{2v}$ symmetry, although cyclopentene has been shown to be non planar, with $C_3$ symmetry. However, slight bending away from planar results in a small perturbation of the $C_{2v}$ selection rules. Hence there are 33 normal vibrations for cyclopentene. Under $C_{2v}$ symmetry, the six A$_2$ vibrations are not infrared active, leaving 27 infrared active vibrational modes. The complete range of vibrations is discussed in more detail in the next Chapter.
Table 3–4: Previous assignments of selected cyclopentene bands, with corresponding symmetry species from [160].

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\tilde{\nu}/\text{cm}^{-1}$</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>liquid [161]</td>
<td>gas [160]</td>
</tr>
<tr>
<td>CH sym. str.</td>
<td>A$_1$</td>
<td>3066(s)$^a$</td>
<td>3078(s)</td>
</tr>
<tr>
<td>CH antisym. str.</td>
<td>B$_1$</td>
<td>3068(s)</td>
<td>3050</td>
</tr>
<tr>
<td>$\alpha$-CH$_2$ antisym. str. (i.p.)</td>
<td>B$_2$</td>
<td>2958(vs)$^a$</td>
<td>2963(s)</td>
</tr>
<tr>
<td>$\beta$-CH$_2$ antisym. str.</td>
<td>B$_2$</td>
<td>2927(vs)$^{a,b}$</td>
<td>2933(s)</td>
</tr>
<tr>
<td>$\beta$-CH$_2$ sym. str.</td>
<td>A$_1$</td>
<td>2902$^c$</td>
<td>2903(s)</td>
</tr>
<tr>
<td>$\alpha$-CH$_2$ sym. str. (o.p.)</td>
<td>B$_1$</td>
<td>2873(s)</td>
<td>2865</td>
</tr>
<tr>
<td>$\alpha$-CH$_2$ sym. str. (i.p)</td>
<td>A$_1$</td>
<td>2852(vs)$^a$</td>
<td>2860(s)</td>
</tr>
<tr>
<td>$\nu$ (C=C)</td>
<td>A$_1$</td>
<td>1619</td>
<td>1623(m)</td>
</tr>
<tr>
<td>$\beta$-CH$_2$ def.</td>
<td>A$_1$</td>
<td>1465</td>
<td>1471(vw)</td>
</tr>
<tr>
<td>$\alpha$-CH$_2$ def. (i.p.)</td>
<td>A$_1$</td>
<td>1445(m)</td>
<td>1445</td>
</tr>
<tr>
<td>$\alpha$-CH$_2$ def. (o.p.)</td>
<td>B$_1$</td>
<td>1445</td>
<td>1438(vw)</td>
</tr>
</tbody>
</table>

$^a$ from [163]
$^b$ assigned as B$_1$
$^c$ assigned as B$_2$
Table 3–5: Position and assignment of selected bands due to cyclopentene from previous surface studies.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>( \tilde{\nu} / \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EELS on Pt(111)</td>
<td></td>
</tr>
<tr>
<td>90K [136]</td>
<td>&lt;250K[136]</td>
</tr>
<tr>
<td>multilayer</td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{CH}) )</td>
<td>3080(w)</td>
</tr>
<tr>
<td>( \nu (\text{CH}_2) )</td>
<td>2975(m) 2970(m)</td>
</tr>
<tr>
<td>( \nu (\text{CH}_2) )</td>
<td>2890(m)</td>
</tr>
<tr>
<td>( \nu (\text{CH}) ) soft</td>
<td>2695-2750(w)</td>
</tr>
<tr>
<td>( \delta (\text{CH}_2) )</td>
<td>1470(m) 1460(m/w)</td>
</tr>
</tbody>
</table>

where a greater spectral range was accessible using RAIRS, rather than only vibrations in the CH stretching region seen with supported metal catalysts.

From the point of view of experiments described in this Chapter, the relevant literature vibrations were listed in Tables 3–4 and 3–5. For cyclopentene adsorbed as a planar molecule, a number of CH vibrations are anticipated. The CH bonds at the two alkene carbon atoms will be parallel to the metal surface and the band intensities may be affected in the presence of the metal. These vibrations would be anticipated above 3000\( \text{cm}^{-1} \). Indeed the bands observed at 3059\( \text{cm}^{-1} \) in DRIFTS and at 3062\( \text{cm}^{-1} \) in transmission are assigned as to a \( \nu \) CH vibration and support the fact that the molecule retains substantial alkene character, and the alkene carbon atoms are not rehybridised from sp\(^2\) to sp\(^3\). The intensity of this band is weak in both studies, and may be reduced from the quoted strong gas phase intensity. This band is seen only briefly on silica as the pulse passes through the sample, and it is brought up in intensity on EuroPt-1 in the presence of the metal, suggesting that it is due to a symmetric vibration.

The observation of A\(_1\) and B\(_2\) vibrations in the DRIFTS spectra of adsorbed cyclopentene suggest that the symmetry of the adsorbed cyclopentene is C\(_2\). On going from C\(_{2v}\) to C\(_2\) symmetry, the B\(_2\) mode becomes A\(^\prime\) and IR al-
allowed. The 2955 and 2850 cm\(^{-1}\) bands observed on EuroPt-1 in DRIFTS are assigned to CH\(_2\) stretching vibrations. Both the symmetric and asymmetric \(\nu\) (CH) vibrations will give rise to an oscillating dipole perpendicular to the metal surface and so if the MSSR holds, the symmetric vibration should be enhanced and the asymmetric vibration attenuated. The enhancement of the 2850 cm\(^{-1}\) band relative to the 2955 cm\(^{-1}\) band on EuroPt-1 is in contrast to the relative intensities observed on silica for the corresponding bands, where the 2957 cm\(^{-1}\) band is more intense than the 2867 cm\(^{-1}\) band. On EuroPt-1, the 2850 cm\(^{-1}\) band is narrower than the other bands. The peaks observed are generally quite broad, of the order of tens of wavenumbers at half height, resulting from sample inhomogeneity and also the inherent spectral linewidth. The shoulder to the 2957 cm\(^{-1}\) band observed on silica probably contributes to the asymmetry of the 2955 cm\(^{-1}\) band on EuroPt-1. The shift of the 2867 cm\(^{-1}\) band on silica to 2850 cm\(^{-1}\) on EuroPt-1 suggests a strong interaction between the cyclopentene and platinum giving rise to this shift, reflected by the estimated heat of desorption/decay discussed later. The contrasting relative intensities of the corresponding bands observed using transmission infrared spectroscopy suggest that the spectrum is dominated by a band little affected by the presence of the metal. However if this was gas phase cyclopentene, it would be swept out of the system in the continuous flow of helium, and the persistence of the band negates this possibility.

In the gas phase spectrum of cyclopentene reported [160], five CH\(_2\) stretching vibrations were observed. These are the \(\alpha\)-CH\(_2\) antisymmetric stretch \(^2\) (in plane) at 2963 cm\(^{-1}\), \(\beta\)-CH\(_2\) antisymmetric stretch at 2933 cm\(^{-1}\), \(\beta\)-CH\(_2\) symmetric stretch at 2903 cm\(^{-1}\), \(\alpha\)-CH\(_2\) symmetric stretch at 2873 cm\(^{-1}\) and \(\alpha\)-CH\(_2\) symmetric stretch (in plane) at 2860 cm\(^{-1}\). The \(\alpha\)-CH\(_2\) antisymmetric stretch (out of plane) is of A\(_2\) symmetry and is infrared forbidden. The strong 2850 cm\(^{-1}\) band can be assigned as the \(\alpha\)-CH\(_2\) symmetric stretch

\(^2\)Here \(\alpha\) refers to the alkene C atoms, and \(\beta\) refers to the C atom opposite the C=C bond
(in plane), of cyclopentene on the metal shifted to lower wavenumber in the presence of the platinum metal on which it is adsorbed. There is a hint of a peak just above this that may be attenuated. The 2923cm\(^{-1}\) shoulder seen on silica may be an antisymmetric band attenuated in the presence of the metal, and is probably encompassed under the 2955cm\(^{-1}\) peak on EuroPt-1. The 2801cm\(^{-1}\) peak has been assigned as an overtone of a CH deformation. The 2801 and 3059cm\(^{-1}\) bands are observed only on EuroPt-1 and are thus due to adsorption on the metal rather than on silica. The results observed from cyclopentene adsorption indicate that the MSSR is holding for EuroPt-1, although it may not hold completely since a high proportion of the particles are \(< 2\)nm diameter, and so the asymmetric band may not be completely attenuated.

The decay of the 2850 and 2955cm\(^{-1}\) bands after each pulse has passed over the catalyst suggests that there is initially a substantial contribution to them from gas phase or weakly adsorbed material, perhaps on the support, particularly for the 2955cm\(^{-1}\) peak which shows the greatest fluctuation in intensity. Some intensity is then lost as this species is swept away in the gas flow. The two other bands, at 3059 and 2807cm\(^{-1}\) show a much steadier increase in intensity, where they are less influenced by gas phase interference or overlap with weakly adsorbed species.

The frequencies of some of the cyclopentene bands varied slightly during the recording of each series of spectra. In the DRIFT cyclopentene / Europt-1 series, the 2955, 2850 and 2801cm\(^{-1}\) bands were of constant frequency (within \(\pm 2\)cm\(^{-1}\) of that quoted). The 3059cm\(^{-1}\) band frequency varied between 3055 and 3061cm\(^{-1}\), although not showing any general trend. During adsorption, the relative intensities of the 3059, 2955, 2850 and 2801cm\(^{-1}\) bands in the DRIFTS spectra of cyclopentene shifted from 1 : 2.3 : 3.5 : 1 at the beginning to 1 : 2.6 : 3.9 : 1.1 after the five pulses.

During TPD from EuroPt-1, there were some noticeable changes in the spectra and shifts in band frequencies. The 3059cm\(^{-1}\) peak frequency ranged from 3057cm\(^{-1}\) to 3061cm\(^{-1}\), increasing throughout the TPD. This may be
indicative of the presence of the cyclopentadienyl species ($C_5H_5$) formed from dehydrogenation, although no supporting vibrations in the CH deformation region can be observed due to the blackout in that region by silica. This is discussed further below.

The decrease in strength of the 2850 cm$^{-1}$ band was used to estimate the activation energy to desorption of cyclopentene from EuroPt-1. As already described, this band is due to cyclopentene adsorbed on the metal rather than on the support. A best fit curve was drawn through the intensity data points, and the equation of this curve was then differentiated to obtain the turning point, from where the rate of decay of the band, $dI/dT$, was a minimum, where $I$ is the band intensity and $T$ is the temperature of the spectrum from which $I$ was measured.

By analogy with Redhead's method of determining the activation energy to desorption from the temperature of the maximum rate of desorption during programmed heating [164], the decrease in intensity of an infrared band can be used to estimate the activation energy to desorption. Assuming that the concentration of a surface species, $n$, is directly proportional to the band intensity, $I$, in an infrared spectrum, and thus using $I$ in the Arrhenius equation,

$$-\frac{dI}{dt} = I^a \nu \exp \left( \frac{E_d}{RT} \right)$$  \hspace{1cm} (3.22)

where $E_d$ is the activation energy
$R$ is the gas constant
$\nu$ is a frequency factor, assumed as $10^{13}$ s$^{-1}$
$\beta$ is the heating rate (K/s)
$T_{max}$ is the temperature where $d^2I/dT^2 = 0$ $a$ is the order of reaction, and
$\beta = dT/dt$, so $dI/dt = \beta \frac{dI}{dt}$, then

$$-\frac{1}{\beta} \frac{dI}{dt} = I^a \nu \exp \left( \frac{E_d}{RT} \right)$$  \hspace{1cm} (3.23)

and

$$-\frac{dI}{dT} = I^a \nu \exp \left( \frac{E_d}{RT} \right)$$  \hspace{1cm} (3.24)

130
and differentiation of the above equation gives

\[- \frac{d^2 I}{dT^2} = \frac{\nu}{\beta} \left[ a I^{a-1} \frac{dI}{dT} \exp \left( -\frac{E_d}{RT} \right) \right] + \left[ \frac{I_a E_d}{RT^2} \exp \left( -\frac{E_d}{RT} \right) \right] \]  \hspace{1cm} (3.25)

where \( d^2 I/dT^2 = 0 \) at \( T_{max} \). Hence

\[- a I^{a-1} \left( \frac{dI}{dT} \right)_{T_{max}} = \frac{I_a E_d}{RT_{max}^2} \]  \hspace{1cm} (3.26)

\[ a I^{a-1} \frac{\nu}{\beta} \exp \left( -\frac{E_d}{RT_{max}} \right) = \frac{E_d}{RT_{max}^2} \]  \hspace{1cm} (3.27)

and if first order desorption is assumed i.e. \( a = 1 \),

\[ \frac{\nu}{\beta} \exp \left( -\frac{E_d}{RT_{max}} \right) = \frac{E_d}{RT_{max}^2} \]  \hspace{1cm} (3.28)

i.e.

\[- \left( \frac{dI}{dT} \right)_{T_{max}} = \frac{I_{T_{max}} E_d}{RT_{max}^2} \]  \hspace{1cm} (3.29)

The plot of \( dI/dT \) is shown in Figure 3–24 and shows \( d^2 I/dT^2 = 0 \) at 403 ± 5 K. This gives an estimate (from the decay of the 2850 cm\(^{-1}\) band) of the activation energy to desorption of 119 ± 2 kJmol\(^{-1}\). However, maxima were observed in the TCD trace at 348K and at 548K, and in the mass spectrometer trace at about 358K. This suggests that cyclopentene is desorbing from the silica support into the gas phase at 348–358K, and that the maximum rate of decay of the 2850 cm\(^{-1}\) infrared band at 403K corresponds to a loss in intensity of the species adsorbed on the metal to other surface species, probably to the two small peaks at 2932 and 2909 cm\(^{-1}\) which come up in intensity at this point, rather than to form gas phase products. In this instance, rather than an activation energy to desorption, this calculation provides an estimate of the activation energy needed for the decay of one surface species to form a new surface species. The peak maximum observed in the TCD trace at 548K corresponds with the decline of these two bands after passing through maximum intensities around 498K, indicating desorption occurs at high temperature. The activation energy of 119 ± 2 kJmol\(^{-1}\) indicates that cyclopentene is strongly held (chemisorbed) on the platinum surface.
As was shown earlier, Avery observed the formation of the cyclopentadienyl species, C₅H₅ or Cp, upon heating adsorbed cyclopentene on Pt(111), using EELS. The observed frequencies, correlated with those for two inorganic complexes, K⁺Cp⁻, and ferrocene, FeCp₂, are listed in Table 3–6, with the symmetry species under D₅d symmetry. Ferrocene can exist in two different forms, staggered and eclipsed with D₅d and D₅h symmetry respectively. The 3059 cm⁻¹ band observed using DRIFTS persists beyond the maximum temperature at which spectra were recorded, 568K, and is perhaps indicative of the symmetrical cyclopentadienyl species since no other bands are appar-
Table 3–6: Frequencies and assignments of selected bands from the cyclopentadienyl species, $C_5H_5$, (Cp) correlated with bands from $K^+Cp^-$ and FeCp$_2$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\nu$ /cm$^{-1}$</th>
<th>EELS 370K[136]</th>
<th>IR K$^+Cp^-$ [165]</th>
<th>IR FeCp$_2$[166]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (CH)</td>
<td>A$_{2u}$</td>
<td>3060</td>
<td>3096$^a$</td>
<td>3085(s)</td>
</tr>
<tr>
<td>$\nu$ (CH)</td>
<td>A$_{1u}$</td>
<td>2990$^b$</td>
<td>3039</td>
<td>3075(s)</td>
</tr>
<tr>
<td>$\nu_{asym.}$ (CC)</td>
<td>E$_{1u}$</td>
<td>1455</td>
<td>1411(s)</td>
<td></td>
</tr>
<tr>
<td>$\nu_{sym.}$ (CC)</td>
<td>A$_{2u}$</td>
<td>1108(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$ (CH)</td>
<td>E$_{2u}$</td>
<td>1033</td>
<td>1002(s)</td>
<td></td>
</tr>
<tr>
<td>$\pi$ (CH)</td>
<td>A$_{2u}$</td>
<td>840</td>
<td>710</td>
<td>811(s)</td>
</tr>
</tbody>
</table>

$a$ Raman active mode

$b$ This band was originally reported at 3010cm$^{-1}$ and adjusted after further study

ent at this point. Indeed in the spectra recorded at 528 and 568K, there is evidence of a weak band at $\sim$3010cm$^{-1}$ agreeing with Avery's observation of CH stretching vibrations due to cyclopentadienyl at 3060 and 2990cm$^{-1}$ 3. All other bands have decayed to zero intensity at this temperature.

On the basis of the observed rate of decay of the 2851cm$^{-1}$ band with increasing temperature, the expected rate of decay of the 3059cm$^{-1}$ band was calculated. A proportionate decrease in the 3059cm$^{-1}$ band intensity was evaluated to give a set of 'calculated' band intensities. This is plotted with the observed (real) band intensities as a function of temperature in Figure 3–25. The higher than calculated intensity of the 3059cm$^{-1}$ band indicates the persistence of a species or presence of the vibration due to some other species with similar $\nu$ at high temperature and supports the fact that it may indeed be due to the presence of the cyclopentadienyl species.

3Initially reported as 3010cm$^{-1}$ but amended to 2990cm$^{-1}$
Figure 3-25: Real and calculated decrease in band intensities during TPD of cyclopentene from EuroPt-1.
Cyclopentene on silica showed two bands, one at 2957 cm\(^{-1}\), which was steady during adsorption but shifted to 2964 cm\(^{-1}\) during TPD, and the other at 2867 cm\(^{-1}\). The 2867 cm\(^{-1}\) peak was not really one distinct maximum, probably due to superimposed noise, and the frequency of the maximum varied between 2858 and 2872 cm\(^{-1}\). TPD showed simple desorption from the silica. During TPD, the position of this band maximum shifted from 2870 cm\(^{-1}\) to 2875 cm\(^{-1}\). The high noise level and indistinct maximum are obvious in Figure 3-39. As was done for the 2850 cm\(^{-1}\) band on EuroPt-1, the decay of the 2957 cm\(^{-1}\) peak was curvefitted and a maximum rate of desorption at 368 ± 5 K gives an estimate of the activation energy to desorption from silica of 108 ± 2 kJmol\(^{-1}\).

The two experiments involving hydrogen pulsing were undertaken to investigate the behaviour observed in the simple TPD experiment described earlier where cyclopentene adsorbed on EuroPt-1 was heated. The 2955 cm\(^{-1}\) peak shifted from its initial position at 2955 cm\(^{-1}\) up to 2978 cm\(^{-1}\) at high temperature. In that experiment, there was a large shift in the \(v\) of that band, from 2955 to 2968 cm\(^{-1}\) between the spectra recorded at 408 and 433 K. Two new peaks emerged out of the initial 2955 cm\(^{-1}\) peak, at 408 K, increasing in intensity and subsequently decreasing at higher temperature. The position of these new peaks was 2932 cm\(^{-1}\) and 2909 cm\(^{-1}\) (initially 2905 and finally 2909 cm\(^{-1}\)). The 2850 cm\(^{-1}\) peak shifted slightly above 498 K with the peak maximum at 2843 cm\(^{-1}\) at 568 K. The 2801 cm\(^{-1}\) peak lost intensity steadily before the other peaks did, without shifting in frequency.

The DRIFTS spectra recorded during the hydrogenation experiments described in Section 3.11.1 show the behaviour of the adsorbed species at 310 K and at 483 K. Following cyclopentene adsorption at 310 K, bands were observed at 3057, 2954, 2851 and 2801 cm\(^{-1}\). As the first pulse of hydrogen passes through the catalyst, the next DRIFTS spectrum shows a dramatic increase in intensity of what was the 2954 cm\(^{-1}\) peak, with two maxima, at 2963 and 2945 cm\(^{-1}\). The peaks at 2963 and 2945 cm\(^{-1}\) correlate well with the \(CH_2\) stretching vibrations of gas phase cyclopentane at 2960 and 2944 cm\(^{-1}\),
as seen in Figure 3–48. There is a concomitant shift in the 2851cm⁻¹ peak to 2857cm⁻¹, and loss in intensity of both the 2081 and 2857cm⁻¹ peaks. The 2857cm⁻¹ peak then remains at this position, present throughout the subsequent spectra recorded. The 3057cm⁻¹ peak immediately lost all intensity and is not present in any subsequent spectra, and the 2801cm⁻¹ peak decays gradually. What was the 2954cm⁻¹ band (now 2945cm⁻¹) shows a brief increase in intensity in the spectrum immediately following the two further hydrogen pulses. Together with the mass spectral and TCD evidence, and from a comparison from the DRIFT spectra of cyclopentane on EuroPt-1, Figure 3–48, and gas phase cyclopentene vibrational frequencies, it can be concluded that pulsing the cyclopentene covered surface at 310K results in the hydrogenation of cyclopentene to cyclopentane on the catalyst surface followed by desorption into the gas phase. Very small amounts of hydrogenation were observed following the two subsequent pulses of hydrogen, and the products were swiftly swept away in the helium flow. Cyclopentane on EuroPt-1 showed a dominant band at 2859cm⁻¹, and another band at 2949cm⁻¹, as shown in Figure 3–48.

In the second hydrogen pulsing experiment, the DRIFTS spectra recorded during adsorption of cyclopentene and prior to heating and pulsing with hydrogen at 483K showed bands at 3057, 2955, 2851 and 2800cm⁻¹. After heating to 483K, bands were observed at 3063, 2967, 2930, 2909 and 2851cm⁻¹. As the catalyst was heated during this series of spectra, again the 3057cm⁻¹ peak shifted to 3063cm⁻¹ perhaps indicating the formation of the cyclopentadienyl species on heating. As the first pulse of hydrogen passed over the catalyst, a shift of the 2930cm⁻¹ band to 2934cm⁻¹ was observed, perhaps indicating the hydrogenation of an unsaturated species. This band subsequently decreased in intensity, along with a decrease in intensity of the 3063cm⁻¹ band (and perhaps the 2851cm⁻¹ band). The 3063cm⁻¹ band vanished after the pulse of hydrogen, perhaps indicating the hydrogenation of the cyclopentadienyl species and desorption from the surface. No persistent band was observed as in the initial TPD experiment discussed earlier. The
effect of further pulses of hydrogen is not shown since peaks have decreased to almost negligible intensities at this point.

The identity of the two small emergent peaks has not been positively established from the surface reaction experiments with hydrogen, although hydrogenation appeared to result, indicating these bands to be due to vibrations of an unsaturated species. They may be due to a dehydrogenated species of $C_5H_n$ or other stoichiometry. Other possibilities include reorientation of the molecule on the surface, or breakup of the $C_5$ ring, but the hydrogenation experiments do not support the possibility of fragmentation. The $3057\text{cm}^{-1}$ band was not evident at high temperature in the hydrogen pulsing experiment, indicating the species responsible is not present on the catalyst in this experiment, as a result of earlier hydrogenation and desorption.

The transmission experiment shows some differences to the DRIFTS experiment. The relative intensities of the $2962$ and $2852\text{cm}^{-1}$ bands observed in transmission are similar to those observed for the $2957$ and $2867\text{cm}^{-1}$ peaks in DRIFTS, suggesting that the intensities in the transmission experiment are not influenced by the metal surface selection rule for some reason, although the shift in frequencies is a result of the interaction with the metal. Perhaps the physical nature of the catalyst has been altered in the manufacture of the disc. The signal to noise ratio is higher in transmission, due to the higher maximum response at $3000\text{cm}^{-1}$ in the single beam spectrum from transmission in the CH stretching region. As shown in Figure 3–17, the maximum response in transmission is $2V$ compared with $0.4V$ in DRIFTS. Despite this disadvantage, DRIFTS shows good sensitivity in the CH stretching region, and experiments with cyclopentane and methylcyclopentane were carried out using DRIFTS rather than transmission.

Similar amounts of catalyst are in the infrared beam path in transmission and DRIFTS although the transmission disc was made up of $\sim75\text{mg}$ of catalyst, and this should be remembered in considering quantitative uptake determined from TCD and mass spectrometry. The transmission TPD
experiment showed a shoulder at slightly lower wavenumber than the 2955 cm\(^{-1}\) peak, at 2931 cm\(^{-1}\), although it is not clearly resolved as in the DRIFTS spectra. Also, a shoulder is apparent at 3037 cm\(^{-1}\), and may be due to the cyclopentadienyl species. The apparently lower desorption temperatures in transmission are due to the thermocouple being sprung against the catalyst disc measuring the temperature at the edge of the disc, while considerable temperature gradients probably exist from there to the heating mesh at the centre of the disc, resulting in much higher actual temperatures at the catalyst than measured by the thermocouple at the edge of the disc. In the DRIFTS cell, the thermocouple is embedded in the catalyst sample and so measures the temperature more accurately.

The frequencies observed for cyclopentene on EuroPt-1 from transmission infrared are all slightly higher than the corresponding DRIFTS frequencies. There may be differing contributions from gas phase or weakly adsorbed species in the two experiments. The 2962 cm\(^{-1}\) band is initially dominant and remains within ±2 cm\(^{-1}\) throughout. The 3062 cm\(^{-1}\) peak is reasonably steady but ranges up to 3067 cm\(^{-1}\) in the first few spectra, probably due to the low signal to noise ratio there. The 2852 cm\(^{-1}\) peak is steady, and the 2806 cm\(^{-1}\) peak shows some variation in frequency, particularly as the first peak tails off and the next pulse arrives at the catalyst, there is a shift of 8 cm\(^{-1}\). In marked contrast with the corresponding DRIFTS spectra, Figure 3–30, the bands observed using transmission infrared are much slower to grow in intensity due to diffusion over the catalyst surface, and the higher signal to noise ratio throughout is obvious. Following the first pulse, the 2962 cm\(^{-1}\) peak is dominant, with only a hint of the other peaks which later emerge. The 2962 cm\(^{-1}\) peak observed in transmission is more symmetrical than the corresponding peak observed in DRIFTS. Following the next pulse, the other three bands appear more clearly, and all bands subsequently increase in intensity with different relative intensities to those observed in DRIFTS, as already described.

An important feature to note is the relative intensities of the various
bands observed in the spectra. To illustrate this, a spectrum of adsorbed cyclopentene in each series following three pulses has been plotted in Figure 3–26. All spectra are plotted on the same intensity scale to illustrate the absolute intensities of bands in the three experiments. The surface area of the silica is 364 m²g⁻¹ compared with the surface area of the catalyst of 165 m²g⁻¹. This factor is also apparent in the greater uptake of hydrocarbon by silica than by EuroPt-1.

The signal to noise levels in the DRIFTS and transmission spectra were markedly different. In the DRIFTS spectra, the mean peak to peak noise level was 0.0003 Absorbance units, in contrast to 0.0001 Absorbance units in the transmission spectra. This gave signal to noise ratios of 12 : 2 : 45 : 12 for the 3059, 2955, 2850 and 2801cm⁻¹ peaks in the DRIFTS spectra and 21 : 59 : 39 : 10 in transmission, for the 3062, 2962, 2852 and 2806cm⁻¹ peaks in the transmission spectra, following three pulses. The relative signal to noise ratio for these peaks in transmission compared with DRIFTS is given by division of these ratios, giving 1.7 : 2.1 : 0.9 : 0.8.

During TPD in the transmission experiment, the 3062cm⁻¹ peak position varies only slightly, and above 433K a small peak at 3037cm⁻¹ is apparent. The 2962cm⁻¹ peak shifts slightly as it loses intensity, to 2954cm⁻¹ at 513K with a small side peak at 2931cm⁻¹ emerging. The 2852cm⁻¹ peak shifts only slightly to 2849cm⁻¹ and the 2806cm⁻¹ peak decays the most rapidly with no noticeable shift in frequency.

3.12.2 Cyclopentane

The band frequencies for adsorbed cyclopentane on EuroPt-1 and silica observed using DRIFTS are listed in Table 3–7, together with their proposed assignment. Some frequencies from related studies and the appropriate symmetry label for gas phase species, under D₅h symmetry , are listed in Table 3–8. As with cyclopentene, the operation of the metal surface selection rule is apparent. The peak due to the CH₂ stretching vibration at 2859cm⁻¹
Figure 3-26: Illustration of cyclopentane band intensities on (a) EuroPt-1 / DRIFTS, (b) Silica / DRIFTS and (c) EuroPt-1 / transmission.
Table 3-7: Position and assignment of bands from cyclopentane on EuroPt-1 and silica.

<table>
<thead>
<tr>
<th>Proposed Assignment</th>
<th>( \tilde{\nu} / \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu (\text{CH}<em>2)</em>{\text{asym}} )</td>
<td>EuroPt-1</td>
</tr>
<tr>
<td>( A'' )</td>
<td>2949(w/m)</td>
</tr>
<tr>
<td></td>
<td>2920(sh)</td>
</tr>
<tr>
<td>( \nu (\text{CH}<em>2)</em>{\text{sym}} )</td>
<td>( E'_1 )</td>
</tr>
<tr>
<td>( 2\delta (\text{CH}_2) )</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-8: Previous assignment of selected vibrational bands due to cyclopentane.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>( \tilde{\nu} / \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu (\text{CH}<em>2)</em>{\text{asym}} )</td>
<td>EuroPt-1</td>
</tr>
<tr>
<td>( A'' )</td>
<td>2960(s)</td>
</tr>
<tr>
<td></td>
<td>2935</td>
</tr>
<tr>
<td></td>
<td>2966</td>
</tr>
<tr>
<td>( \nu (\text{CH}<em>2)</em>{\text{sym}} )</td>
<td>( E'_1 )</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{CH}_2) ) soft</td>
<td>2320-2880(vs)</td>
</tr>
<tr>
<td>( \delta (\text{CH}_2) )</td>
<td>( E'_1 )</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is enhanced on EuroPt-1 relative to the band due to the \( \text{CH}_2 \) asymmetric stretch at 2949 cm\(^{-1}\). The relative intensities of the 2870 and 2957 cm\(^{-1}\) bands observed on silica are reversed on EuroPt-1 after three pulses with the 2859 cm\(^{-1}\) peak dominant.

The adsorption of cyclopentane on EuroPt-1 showed bands with vibrational frequencies in good agreement with previous surface studies and with liquid cyclopentane. The band at 2949 cm\(^{-1}\) was only briefly observed following a pulse, and then lost intensity as the 2859 and 2804 cm\(^{-1}\) bands maintained or actually increased their intensities after a pulse had passed through the catalyst. These bands are assigned as the \( \nu \text{CH}_2 \) (antisymmetric) stretching vibration at 2949 cm\(^{-1}\) and \( \nu \text{CH}_2 \) (symmetric) stretching vibration at 2859 cm\(^{-1}\), and their shift to lower wavenumber from that of liquid cyclopentane and from those observed on silica at 2957 and 2870 cm\(^{-1}\), indicate the influence of the metal on the vibrational frequencies.
The reversal in relative intensities of the 2949 and 2859 cm\(^{-1}\) bands from that observed for the 2957 and 2870 cm\(^{-1}\) bands on silica again indicate the enhancement of the symmetric vibration and attenuation of the anti-symmetric vibration in the presence of the metal, thus the operation of the metal surface selection rule. Overall, the band intensities are weaker for cyclopentane than for cyclopentene. There was no sign of any soft bands such as those observed by Avery for cyclopentane adsorbed on Pt(111), and this is further investigated in the RAIRS study of cyclopentane on Pt(111) in the next Chapter. TPD shows uncomplicated decay in band intensities at lower temperature than observed for cyclopentene, indicating molecular desorption without dehydrogenation or decomposition.

The frequency of the 2949 cm\(^{-1}\) band on EuroPt-1 varied between 2947 and 2953 cm\(^{-1}\), and the 2859 cm\(^{-1}\) band was steady as was the 2804 cm\(^{-1}\) peak. During TPD, there was little variation in any of the peak frequencies. TPD of cyclopentane from EuroPt-1 gave a maximum rate of decay of the 2859 cm\(^{-1}\) band at 363 \(\pm\) 5 K corresponding to an activation energy to desorption, calculated as described for cyclopentene, of 106 \(\pm\) 2 kJ mol\(^{-1}\).

On silica, bands were all at the quoted frequency, or within \(\pm\) 2 cm\(^{-1}\). The maximum rate of decay of the 2957 cm\(^{-1}\) band from cyclopentane on silica was at 328 \(\pm\) 5 K, corresponding to an activation energy to desorption of 96 \(\pm\) 2 kJ mol\(^{-1}\). A spectrum from each series of spectra following adsorption of cyclopentane on EuroPt-1 and on silica is plotted in Figure 3–27 for comparison, showing cyclopentane to be held slightly more strongly on EuroPt-1 than on silica.

### 3.12.3 Methylcyclopentane

The frequency of bands observed for methylcyclopentane adsorbed on EuroPt-1 and on silica are listed in Table 3–9, along with their assignment. No CH vibration, for the H attached to the carbon to which the methyl group is also attached, was seen for methylcyclopentane above 3000 cm\(^{-1}\), proba-
Figure 3-27: DRIFTS spectra of cyclopentane adsorbed on (a) EuroPt-1 and (b) silica.
Table 3-9: Position and assignment of bands from methylcyclopentane on EuroPt-1.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>ν/cm⁻¹</th>
<th>EuroPt-1</th>
<th>silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(CH₂)_{asym}</td>
<td>2946</td>
<td>2954</td>
<td></td>
</tr>
<tr>
<td>ν(CH₃)_{sym}</td>
<td>2907</td>
<td>2912 (sh)</td>
<td></td>
</tr>
<tr>
<td>ν(CH₂)_{sym}</td>
<td>2855</td>
<td>2869</td>
<td></td>
</tr>
<tr>
<td>2δ(CH₂)</td>
<td>2808</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

bly as it was too weak to be observed. The DRIFTS spectra of cyclopentane and methylcyclopentane on silica are very similar, but on EuroPt-1 they are markedly different. The 2855cm⁻¹ band becomes dominant and is brought up in intensity in the presence of the metal along with the 2907cm⁻¹ band, compared with the corresponding spectra of cyclopentane on EuroPt-1. The 2808cm⁻¹ band is only seen on the catalyst, and is an overtone or combination band, again brought up in intensity in the presence of the metal.

The bands observed following methylcyclopentane adsorption were assigned on the basis of the cyclopentane spectra observed and from the literature cyclopentane frequencies, with the knowledge of the presence of an additional methyl group. By analogy with cyclopentane, the 2946cm⁻¹ band was assigned to the antisymmetric CH₂ stretching vibration, the 2855cm⁻¹ band to the symmetric CH₂ stretching vibration and the additional band at 2907cm⁻¹ to the CH vibrations within the methyl group. The downshifting of these three peaks from the frequencies observed on silica is due to the presence of the metal. Again, a shift in relative intensities on EuroPt-1 was observed after the pulse had passed through the catalyst, as the 2946cm⁻¹ peak lost intensity and the 2907 and 2855cm⁻¹ peaks remained steady or gained intensity. This behaviour is similar to that observed for cyclopentane, but in contrast to that seen for cyclopentene. Following the three pulses, the 2855cm⁻¹ band was dominant with respect to the 2946cm⁻¹ peak, contrasting with the corresponding peaks on silica. A spectrum of each of
methylcyclopentane and of cyclopentane adsorbed on EuroPt-1 is shown in Figure 3-28 for comparison.

![DRIFTS spectra of (a) methylcyclopentane and (b) cyclopentane adsorbed on EuroPt-1](image)

Figure 3-28: DRIFTS spectra of (a) methylcyclopentane and (b) cyclopentane adsorbed on EuroPt-1

As for cyclopentene, enhancement of the 2855cm⁻¹ peak and of the 2907cm⁻¹ peak, the symmetric CH₂ and CH₃ stretching vibrations, with respect to the 2946cm⁻¹ band illustrates the operation of the metal surface selection rule. These relative intensities are in contrast with the relative intensities observed on silica. As for the other molecules, a spectrum from each of the series of adsorption on EuroPt-1 and on silica is shown in Figure 3-29 for comparison.

There is noise superimposed on the EuroPt-1 spectra, but the behaviour of the peak maxima can be discerned. The 2946cm⁻¹ peak frequency is steady, the 2907cm⁻¹ peak varies from 2912cm⁻¹ to 2906cm⁻¹ due to the noise, and the other peaks remain at constant frequency. During TPD, the 2907cm⁻¹ peak shifts to 2891cm⁻¹ and the 2855cm⁻¹ peak shifts to 2847cm⁻¹.
Figure 3–29: Illustration of the differences between a DRIFTS spectrum of methylcyclopentane adsorbed on (a) EuroPt-1 and (b) silica.
at 423K, and the 2808cm\(^{-1}\) peak is at constant frequency. The maximum rate of decrease of the 2855cm\(^{-1}\) peak during the TPD of methylcyclopentane from EuroPt-1 was observed at 363 ± 5 K, corresponding to an activation energy to desorption, calculated in the same way as before, of 106± 2 kJmol\(^{-1}\)

On silica, the peak frequencies are constant throughout adsorption and TPD. Desorption of methylcyclopentane from silica shows a maximum rate of decrease of the 2954cm\(^{-1}\) band at 328 ± 5 K giving an activation energy to desorption of 96 ± 2 kJmol\(^{-1}\), similar to that for the desorption of cyclopentane from silica.

### 3.13 Summary

The infrared study of the adsorption of three cyclic hydrocarbon molecules on EuroPt-1 and on silica has shown the suitability of DRIFTS in studying vibrations in the \(\nu\) (CH) region. The bands observed could be assigned to particular vibrations with reference to literature spectra and to previous surface studies. The variation in intensity of infrared bands was used to monitor the adsorption and desorption/decay of bands/ species. In conjunction with TCD and mass spectral analysis of the gas phase, quantitative information was determined. The uptake of hydrocarbon from each pulse injected into the flow system was determined from the integrated area under TCD peaks. Analysis of the gas phase with the mass spectrometer revealed the composition of the products following adsorption and reaction. The decay in intensity of IR bands allowed an estimation of the activation energy to desorption, so revealing the strength of the interaction of the adsorbate with the catalyst. The infrared bands observed are summarised with their assignment in Table 3-10.

The strongest interaction was for cyclopentene, which also showed a considerable difference in the activation energy to desorption/decay of species from silica and from the metal. The small difference in the figures for both
Table 3–10: Summary of DRIFTS vibrational frequencies determined in this study.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>cyclopentene</th>
<th>cyclopentane</th>
<th>methylcyclopentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (CH)</td>
<td>3059(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$ (CH$<em>2$)$</em>{\text{asym}}$</td>
<td>2955(w)</td>
<td>2949(w/m)</td>
<td>2946(w/m)</td>
</tr>
<tr>
<td>$\nu$ (CH$<em>3$)$</em>{\text{sym}}$</td>
<td></td>
<td>2907(w/m)</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (CH$<em>2$)$</em>{\text{sym}}$</td>
<td>2850(s)</td>
<td>2859(m)</td>
<td>2855(m)</td>
</tr>
<tr>
<td>2$\delta$ (CH$_2$)</td>
<td>2801(w)</td>
<td>2804(w)</td>
<td>2808(w)</td>
</tr>
</tbody>
</table>

The alkanes studied is consistent with the metal-alkane interaction being weaker than the metal-alkene interaction, reflected by the difference in the activation energy to desorption for the alkanes studied and for cyclopentene. The main figures extracted for the collated data are summarised in Table 3–11.

TPD of cyclopentene resulted in formation of new bands, and although their identity has not been established, temperature programmed experiments with hydrogen indicate that hydrogenation occurs. Cyclopentane and methylcyclopentane showed simpler chemistry on the surface, and desorbed molecularly on heating.
Table 3-11: Summary of data obtained in the study of adsorption on EuroPt-1

<table>
<thead>
<tr>
<th>Molecule</th>
<th>cyclopentene</th>
<th>cyclopentane</th>
<th>methyl-cyclopentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>uptake EPt-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μmoles</td>
<td>0.35&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>uptake silica</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μmoles</td>
<td>0.6</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>uptake EPt-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>transmission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPt-1</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EA/kJmol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>119&lt;sup&gt;b&lt;/sup&gt;</td>
<td>106</td>
<td>106</td>
</tr>
<tr>
<td>silica</td>
<td>108</td>
<td>96</td>
<td>96</td>
</tr>
</tbody>
</table>

<sup>a</sup> Uptake from 5 pulses, all others from 3 pulses

<sup>b</sup> Activation energy to decay rather than desorption
Figure 3-30: DRIFTS spectra recorded during cyclopentene adsorption on EuroPt-1 at 310K (3150 → 2750 cm\(^{-1}\)).
Figure 3–31: DRIFTS spectra recorded during cyclopentene adsorption on EuroPt-1 at 310K (3150 → 2750cm⁻¹) contd. from previous page.
Figure 3–32: Strength of absorption bands as a function of time during cyclopentene adsorption on EuroPt-1, from DRIFTS spectra in Figures 3–30 and 3–31.
Figure 3-33: DRIFTS spectra recorded during TPD following cyclopentene adsorption on EuroPt-1 (3150 → 2750 cm⁻¹).
Figure 3-34: Expanded plots of the final two spectra during TPD of cyclopentene from EuroPt-1, (a) 548K and (b) 568K (3150 → 2750 cm\(^{-1}\)).
Figure 3–35: Strength of absorption bands as a function of temperature during TPD of cyclopentene from EuroPt-1, from DRIFTS spectra in Figure 3–33.
Figure 3–36: DRIFTS spectra recorded during H₂ pulsing at 310K following cyclopentene adsorption on EuroPt-1 (3150 → 2750 cm⁻¹).
Figure 3-37: Strength of absorption bands as a function of spectrum number during hydrogen pulsing of cyclopentene on EuroPt-1, from DRIFTS spectra in Figure 3-36.
Figure 3-38: DRIFTS spectra recorded during $\text{H}_2$ pulsing following cyclopentene adsorption on EuroPt-1 and then heating to 483K ($3150 \rightarrow 2750\text{cm}^{-1}$).
Figure 3–39: DRIFTS spectra recorded during cyclopentene adsorption on silica at 309K (3150 → 2750 cm⁻¹).
Figure 3-40: Strength of absorption bands as a function of time during cyclopentene adsorption on silica, from DRIFTS spectra in Figure 3-39.
Figure 3-41: DRIFTS spectra recorded during TPD following cyclopentene adsorption on silica (3150 → 2750 cm⁻¹).
Figure 3–42: Strength of absorption bands as a function of temperature during TPD of cyclopentene from silica, from DRIFTS spectra in Figure 3–41.
Figure 3-43: Transmission infrared spectra recorded during cyclopentene adsorption on EuroPt-1 at 310K (3150 → 2750cm⁻¹).
Figure 3-44: Strength of absorption bands as a function of time during cyclopentene adsorption on EuroPt-1, from transmission spectra in Figure 3-43.
Figure 3-45: Transmission infrared spectra recorded during TPD following cyclopentene adsorption on EuroPt-1 (3150 → 2750cm\(^{-1}\)).
Figure 3-46: Expanded plot of 463K spectrum in series of transmission TPD spectra of cyclopentene on EuroPt-1 (3150 → 2750 cm\(^{-1}\)).
Figure 3-47: Strength of absorption bands as a function of temperature during TPD of cyclopentene from EuroPt-1, from transmission spectra in Figure 3-45.
Figure 3-48: DRIFTS spectra recorded during cyclopentane adsorption on EuroPt-1 at 309K (3050 → 2750cm⁻¹).
Figure 3-49: Strength of absorption bands as a function of time during cyclopentane adsorption on EuroPt-1, from DRIFTS spectra in Figure 3-48.
Figure 3–50: DRIFTS spectra recorded during TPD following cyclopentane adsorption on EuroPt-1 (3050 → 2750 cm$^{-1}$).
Figure 3-51: Strength of absorption bands as a function of temperature during TPD of cyclopentane from EuroPt-1, from DRIFTS spectra in Figure 3-50.
Figure 3-52: DRIFTS spectra recorded during cyclopentane adsorption on silica at 308K (3050 → 2750 cm\(^{-1}\)).
Figure 3–53: Strength of absorption bands as a function of time during cyclopentane adsorption on silica, from DRIFTS spectra in Figure 3–52.
Figure 3–54: DRIFTS spectra recorded during TPD following cyclopentane adsorption on silica (3050 → 2750 cm⁻¹).
Figure 3–55: Strength of absorption bands as a function of temperature during TPD of cyclopentane from silica, from DRIFTS spectra in Figure 3–54.
Figure 3-56: DRIFTS spectra recorded during methylcyclopentane adsorption on EuroPt-1 at 309K (3050 → 2750 cm⁻¹).
Figure 3-57: Strength of absorption bands as a function of time during methylcyclopentane adsorption on EuroPt-1, from DRIFTS spectra in Figure 3-56.
Figure 3-58: DRIFTS spectra recorded during TPD following methylcyclopentane adsorption on EuroPt-1 (3050 → 2750 cm⁻¹).
Figure 3–59: Strength of absorption bands as a function of temperature during TPD of methylcyclopentane from EuroPt-1, from DRIFTS spectra in Figure 3–58.
Figure 3-60: DRIFTS spectra recorded during methylcyclopentane adsorption on silica at 308K (3050 → 2750 cm⁻¹).
Figure 3-61: Strength of absorption bands as a function of time during methylcyclopentane adsorption on silica, from DRIFTS spectra in Figure 3-60.
Figure 3-62: DRIFTS spectra recorded during TPD following methylcyclopentane adsorption on silica (3050 → 2750 cm⁻¹).
Figure 3-63: Strength of absorption bands as a function of temperature during TPD of methylcyclopentane from silica, from DRIFTS spectra in Figure 3-62.
Chapter 4

RAIRS Study of Adsorption of Cyclic Hydrocarbons on Pt(111)

4.1 Introduction

The form of infrared spectroscopy discussed in this Chapter is that of Reflection Absorption Infrared Spectroscopy, known as RAIRS or sometimes as IRAS (Infrared Reflection Absorption Spectroscopy). In contrast to DRIFTS and transmission infrared spectroscopy discussed in the preceding Chapter, RAIRS is applicable to macroscopic planar metal surfaces rather than to the high surface area supported metals described earlier.

The technique has developed to its current status as one of the most useful ways of investigating catalytic behaviour on model catalyst surfaces from initial studies back in 1959. Monolayers of hydrogen and CO were studied on metal film mirrors and Langmuir-Blodgett films on silver were also investigated [169]. In the initial RAIRS experiments, multiple reflection of the infrared beam from polycrystalline surfaces incident at near grazing incidence was used in order to obtain sufficient sensitivity [170-174]. Greenler subsequently investigated the conditions for optimum absorbance using the multiple reflection technique, both experimentally [173], and theoretically.
He showed that in fact the optimum angle of incidence is close to grazing. Greenler’s conclusions provide the basis of the RAIRS experiment.

With the development of vacuum technology and surface science in the 1960s, RAIRS was applied to more well defined surfaces, firstly to UHV-prepared metal films and subsequently to the single crystal substrates used today. The first reported RAIRS observation on a single crystal surface was of CO on copper, in 1972 [176]. Since then, many RAIRS experiments have been reported using both metal and semiconductor substrates. Many review articles on the technique have been published [177-180, 133].

Studies were initially made of CO adsorption since it is a strong infrared chromophore, and now the more weakly absorbing hydrocarbons can be routinely investigated. Typical absorption by a CO monolayer on a 1cm² single crystal is of the order of 2–3%, and for a hydrocarbon ~0.01%.

4.2 The Physical Basis of RAIRS

The physical basis of reflection absorption infrared spectroscopy is summarised below. For a molecule adsorbed on a metal surface, its interaction with radiation is dominated by the dielectric behaviour of the metal as the electric field of the infrared beam and the dipole moment of the molecular vibration both interact with the metal electrons. The conditions for a RAIRS experiment must be optimised to achieve sufficient sensitivity since only a small number of vibrations can be observed due to the limited area of the single crystal surface. This is typically 1cm² for a single crystal, compared with the hundreds of square metre surface areas of supported metal catalysts.

Francis and Ellison [181] first recognised that only the p-polarised component of the incident infrared radiation could interact strongly with an adsorbate, and this interaction was enhanced at high angles of incidence. They also investigated the effect of the metal on the absorption of infrared radiation by adsorbates. Greenler quantified these factors [175] using a
classical electrodynamic and therefore macroscopic model, as outlined below. This theoretical model forms the basis of the RAIRS experiment. Subsequently, several other theoretical treatments have been published [173, 182-185]. For an infrared beam incident on a clean highly reflecting metal surface, it may be resolved into s- and p-polarised components in which the electric field vector oscillation is perpendicular and parallel to the plane of incidence respectively. This is shown by $E_s$ and $E_p$ in Figure 4–1. $E_0$ and $E$ are the incident and reflected amplitudes respectively. The p-component

![Figure 4–1: Illustration of the electric vectors of the p- and s-components of the infrared beam on a metal surface, from [178].](image)

can be resolved into components parallel and perpendicular to the surface, as shown by $E_{p||}$ and $E_{p\perp}$ respectively in Figure 4–2. The phase shift of the s- and p-components upon reflection at the surface is considerably different, and is illustrated by $E_s'$ and $E_p'$. The phase of the s-component undergoes a shift of almost 180° on reflection, for all angles of incidence, $\theta$ ($\theta$ is the angle between the incident beam and the surface normal), resulting in the electric vector of the s-component tangential to surface for all $\theta$. This results in a surface field close to zero since the reflection coefficient of metals is close to unity at infrared frequencies. Hence, the s-component of the infrared beam cannot interact significantly with adsorbates. The p-polarised component of the radiation undergoes a phase change strongly dependent on the angle of incidence. As $\theta$ increases, the electric field vector of the p-component (which was tangential for $\theta = 0$), acquires an increasing component normal to
Figure 4-2: Illustration of the parallel and perpendicular components of the p-polarised beam, from [180].

the surface giving a surface electric field varying with angle of incidence as illustrated in Figure 4–3, shown for copper at 2000cm$^{-1}$. At $\theta = 90^\circ$ the surface electric field drops sharply to zero. The profile is similar for all metals reflecting in the infrared. This figure shows that the effective field perpendicular to the surface, $E_{p\perp}$, is almost doubled at high angles of incidence whilst that parallel to the surface, $E_{p\parallel}$, remains small for all angles of incidence. $E_s$ is also shown, showing the very small surface field resulting from the s-component of the infrared beam. Hence, the p-component of the radiation can create a significant field normal to the surface which can interact strongly with vibrations which have a dynamic dipole or component thereof oscillating perpendicular to the surface. This is the origin of the metal surface selection rule [114], that vibrations normal or with component a normal to the surface may be observed on a metal surface. This was discussed in the context of small metal particles in supported metal catalysts in the previous Chapter, and illustrated using the image dipole argument. It results from the screening effect of the metal conduction electrons preventing a tangential field being established at the metal surface. This was further investigated by Greenler [115]. The selection rule has been observed to op-
Figure 4-3: Amplitudes of electric field components relative to $E_0$ (the incident amplitude) as a function of the angle of incidence, $\theta$, for copper at 2000cm$^{-1}$, from [178].

erate in RAIRS [175] and in RAIRS spectra for a multilayer (25nm thick) copper oxalate film on a copper surface [186], as well as in EELS [187]. The area of the surface over which the enhanced field is effective increases as $1/\cos\theta$ for a given incident beam width. Hence, assuming that the intensity of absorption is proportional to $E_0^2$ [188], the intensity of absorption by a surface layer experiencing the field will depend on $\theta$ as $E_0^2 \sec \theta$ ($\sec \theta = 1 / \cos \theta$). This variation in intensity plotted as $(E/E_0)^2 \sec \theta$ as a function of $\theta$ is shown in Figure 4-4 for s-, p$_\perp$ and p$_\parallel$. This function shows a sharp peak near grazing incidence, and has been confirmed experimentally for CO on copper films [189]. The enhancement at the optimum angle of incidence is very large with highly reflecting metals, of the order of twofold. However, in practice, the intensity enhancement can be limited. The physical size of a single crystal is too small to take full advantage of the $\sec \theta$ dependence since at high angles of incidence, the image from the source is likely to cover an area larger than the single crystal. Also, the solid angle covered by the
infrared beam from a thermal source necessarily results in some radiation incident on the crystal away from the optimum angle.

The preceding discussion was concerned with reflection from a clean metal surface i.e. a two phase system. However, when an adsorbate is present on the metal surface, its optical properties must also be considered, particularly its refractive index. Greenler [175] extended the two phase macroscopic model to a three phase system as shown in Figure 4–5. $n_1$ is the refractive index in the vacuum, and similarly $n_2$ and $n_3$ are the respective refractive indices of the adsorbate layer and of the metal. In this model, the adsorbate layer is considered as an isotropic dielectric, and in its presence, the absorption is reduced by a factor of $n_2^2$, where $n_2$ is the refractive index of the adsorbate layer, although the overall profile of the curve shown in Figure 4–4 is retained [190]. McIntyre and Aspnes derived the same conclusions from analytical expressions for the relative change in reflectance ($\Delta R/R$) for a film of thickness d and complex refractive index n-ik [185]. Greenler
Figure 4–5: Illustration of reflection from an adsorbate covered surface, from [180].

defined an absorption function $A = \Delta R/R^\circ$ where $\Delta R = R^\circ - R$, and $R^\circ$ is the reflectance in the three phase system with a non absorbing adsorbate and $R$ is the reflectance of the model adsorbate as shown in Figure 4–6. $A$ is more representative of the absorption peak than the difference between reflectance of the film covered and bare surfaces.

The main theoretical points forming the experimental ground rules for the RAIRS experiment are summarised below;

- Only the p-polarised component of the infrared radiation can interact with the adsorbate
- Only vibrations with a finite component of the dynamic dipole moment perpendicular to the surface are infrared active
- The RAIRS experiment is most efficient at high angles of incidence, i.e. near grazing, typically $\sim 85^\circ$
- The most highly reflecting surfaces give rise to the highest absorbances

As discussed earlier, initial RAIRS experiments were carried out using multiple reflections in order to increase the number of interactions between...
the infrared beam and the absorbers, and thus to increase the intensity of absorption bands. Greenler considered theoretically the advantages of using multiple reflections [173, 175]. In the case of sensitivity being limited by detector noise, there is a loss in total intensity at each reflection as a result of the imperfect reflectivity of the substrate. Hence, there is an optimum number of reflections that maximises \( \Delta R \), at the point where the reflected intensity is lower than the initial incident intensity by a factor of \( e \) [173]. Figure 4–7 shows how the intensity of an absorption band varies as the number of reflections, \( N \), for \( R^* = 0.80 \) and \( R = 0.75 \). This figure shows the maximum absolute absorption intensity for four reflections, with the absorption intensity decreasing with further reflections. Greenler showed that for most metals, a large fraction of the optimised signal could be obtained from a single reflection, and subsequently, all RAIRS studies have been carried out using a single reflection. The potential gain in absorbance with further reflections is outweighed by the practical difficulties in implementing multiple reflections, particularly when using UHV systems equipped for RAIRS and other associated techniques.
4.3 Further Experimental Considerations

Since the number of adsorbate molecules on a typical single crystal surface is small, typically $10^{14}-10^{15}$ at monolayer coverage, it is essential to maximise the detected signal from the limited number of oscillating dipoles. This is even more important at sub-monolayer coverage and for weakly absorbing hydrocarbon molecules. Signal to noise ratios allowing detection of absorptions of $<0.1\%$ are required. This is in stark contrast to DRIFTS and transmission infrared discussed earlier where there are $10^{18}-10^{19}$ adsorbate molecules in the infrared beam path, and sensitivity is not such a problem.

The infrared source used is typically a thermal emitter source, although infrared lasers and infrared synchrotron radiation can be used. As described briefly in Chapter 3, one type of thermal source is a Nernst Globar which is a silicon carbide rod heated to 1100K, mounted in a water cooled housing for...
stability and to increase the source lifetime. It is close to a blackbody source, and the actual power output of the source is relatively low, typically $10^{-7}$ Watts at a few wavenumbers resolution. It is because of the relatively weak output power of thermal sources that attention is turning to high power tunable infrared lasers and high intensity synchrotron sources [191].

To maximise the signal to noise ratio achievable, the various sources of noise must be considered and minimised. Noise can be divided into several sources, firstly detector noise originating from Johnson noise in the detector and preamplifier. There is also source limited noise, sometimes known as shot or photon noise. This arises from the fluctuation of the power of thermal sources resulting from the random nature of spontaneous emission. Noise can also arise from experimental fluctuations, such as changes in the atmosphere of the optical path, changes in optical alignment and mechanical vibration of the crystal and detector. Such drifts can be minimised by mounting the entire spectrometer and associated UHV system on vibration free tables, and isolating or damping noise such as that due to mechanical rotary pumps. The infrared beam can be enclosed within a controlled environment and purged with dry air or evacuated along with the optical bench. This also serves to eliminate absorption bands due to atmospheric H$_2$O and CO$_2$.

Normally, RAIRS spectra are obtained by recording a spectrum of the clean substrate and subsequently recording a spectrum with the adsorbate present, and then ratioing the two spectra to obtain that due to the adsorbate alone. The RAIRS spectrum is thus obtained in a similar way to the DRIFT and transmission spectra presented earlier, but a considerably greater number of scans must be collected to obtain satisfactory sensitivity in the RAIRS spectrum. This results in typical collection times of over 20 minutes for a several thousand scan RAIRS spectrum at 4cm$^{-1}$ resolution compared with 25 seconds for a 50 scan DRIFT or transmission spectrum. The $\sqrt{n}$ advantage obtained by recording $n$ scans in FTIR must be balanced against any further noise introduced over the timescale of recording $n$ scans. Long term
fluctuations adding to the detected noise level are generally more critical with dispersive instruments, and should not be too much of a problem with Fourier Transform (FT) instruments such as used in this study.

Residual drift contributing to noise can be overcome using modulation techniques. The main purpose of modulation is to separate using phase locked detection the actual signal from superimposed noise, intensity fluctuations and background. In the study described below, no modulation was required. However, polarisation modulation which exploits the fact that only the p-polarised radiation interacts with adsorbed molecules, can be used to subtract out gas phase bands when RAIRS spectra are recorded at higher pressures. By switching between s- and p-polarised light using a rotating polariser, the s-component can be used as a reference beam [192, 193].

To achieve maximum sensitivity in a RAIRS experiment, the limiting factor should be detector noise. Typical detectors used in RAIRS are cooled photoconductive or photovoltaic detectors with low noise levels. Liquid helium cooled Germanium bolometer detectors can be used, offering very low noise levels and uniform responsivity over almost the entire infrared range. However, the use of such detectors adds considerably to the complexity of the experiment, and more often the liquid nitrogen cooled semiconductor detectors are employed.

One of the first reported uses of FT-RAIRS was by Low and McManus [174], although most early RAIRS experiments used dispersive spectrometers. Both FT and dispersive techniques have been compared [194, 195], with the conclusion that FTIR offers many advantages over dispersive techniques for RAIRS. FT instruments are insensitive to changes in source intensity and detector responsivity which contribute to the long term drifts associated with dispersive instruments.
4.4 Comparison of RAIRS and EELS

As well as RAIRS, some other techniques have been developed to allow the study of molecular vibrations of molecules adsorbed on well defined metal surfaces. The other main techniques used are Surface Enhanced Raman Scattering (SERS), the main drawback of which is the very limited number of metal surfaces to which it can be applied, and Electron Energy Loss Spectroscopy (EELS) which is the principal 'competitor' to RAIRS. This technique involves reflection of a monoenergetic beam of low kinetic energy electrons (2–5eV) from a flat metal surface. The electrons lose kinetic energy in exciting molecular vibrations thus giving rise to absorption bands in the vibrational spectrum.

The development of EELS preceeded that of RAIRS, with pioneering work done by Propst and Piper who reported the first vibrational spectra from a single crystal substrate, [CO -on W(100)] in 1967 [196]. At that time the resolution attainable was 50 meV(400cm\(^{-1}\)) \(^1\), and improvement in instrumentation followed [197] leading to the establishment of EELS as a powerful vibrational spectroscopy in the mid 1970s. The EELS technique has been the subject of many reviews [197-199], and EELS and RAIRS have often been compared and contrasted [187, 200-203] Even today, each technique has advantages and limitations, which are summarised in Table 4–1. The figures quoted are those that are routinely achievable, and are not state of the art figures. For example, Ibach has recently developed an EELS spectrometer capable of operation at 16cm\(^{-1}\) resolution [204], and this promises to continue the development of the two techniques.

In many respects, the two techniques are complementary. EELS suffers from the main disadvantages of limited resolution and its inability to operate

\(^1\)1meV = 8cm\(^{-1}\)
Table 4–1: Summary of the main advantages and limitations of RAIRS and EELS.

<table>
<thead>
<tr>
<th>Technique</th>
<th>RAIRS</th>
<th>EELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>1cm(^{-1})</td>
<td>40cm(^{-1})</td>
</tr>
<tr>
<td>Pressure Range</td>
<td>UHV (\rightarrow) atm.</td>
<td>(&lt;10^{-6}) mbar</td>
</tr>
<tr>
<td>Spectral Range</td>
<td>4000–1000cm(^{-1})</td>
<td>5000–100cm(^{-1})</td>
</tr>
</tbody>
</table>

at ambient pressure. In contrast, RAIRS can operate easily down to the natural linewidth of surface bands (2–4 cm\(^{-1}\) in ideal conditions). Any small shift of bands with coverage or during reaction can be easily detected. RAIRS can operate at high pressures approaching those of real catalytic reactions, and used with polarisation modulation as already described to subtract gas phase bands where they become significant. However, one of the main advantages EELS has over RAIRS is that the wavelength region that can be usefully covered is larger. At low wavenumber, RAIRS is limited by the low intensity of infrared sources in this region and by the available detection range, and usually vibrations below 850cm\(^{-1}\) cannot be observed using a 'standard' detector. But EELS can detect vibrations down to 100cm\(^{-1}\). In EELS, the angle of incidence of the electron beam is typically 30–45°, and observation near the specular direction (where the angle of incidence and reflection are equal) reveals dipole excitations subject to the metal surface selection rule described earlier. Off specular (impact) observation reveals those vibrations not restricted by the metal surface selection rule. Hence a combination of observations can reveal those bands forbidden in RAIRS. An advantage that RAIRS normally has over EELS is that the crystal is usually heated resistively \textit{in situ} whereas this gives rise to problems in EELS as the electric field created by the heater would deflect the low energy electrons. For this reason, EELS spectra are usually recorded after heating and recooling the crystal. However, this problem can be overcome using another form of heating \textit{e.g.} irradiating the back of the crystal, but this adds to the complexity of the EELS experiment. RAIRS spectra can also
be compared directly with results from supported metal catalysts recorded using other forms of infrared spectroscopy.

4.5 Survey of RAIRS studies of hydrocarbon adsorption

The majority of reported RAIRS studies on single crystal metal surfaces have involved CO as the adsorbate. This is mainly because CO is a strong infrared absorber and can be easily handled in a UHV system. These studies have been summarised and discussed many times [177, 178, 180]. CO has proved to be a useful probe molecule since it is a strong infrared chromophore due to its high dipole moment, and it can adsorb molecularly in distinct linear (on-top) sites, and bridging sites, bonded to two or three surface metal atoms. CO in each of these locations has a distinct vibrational frequency that can be distinguished using high resolution infrared spectroscopy.

However, the object of this study was to investigate more weakly absorbing hydrocarbon molecules on a metal single crystal surface, and some RAIRS results obtained from recent hydrocarbon studies are discussed below. The first reported RAIRS studies of hydrocarbon molecules adsorbed on a single crystal metal surface were of cyclohexane on Cu(111) in 1986 [34] and on Cu(100) [35]. The adsorption of benzene on Pt(111) was also studied using RAIRS in 1986 [36]. One of the most studied species, ethylidyne, which is formed following ethene adsorption, has been observed many times using RAIRS [32, 39, 33, 205-207]. These RAIRS studies followed observation of the ethylidyne species on various metals using EELS and other techniques [33]. Adsorption of the series of C₂ to C₆ straight chain alkanes has also been investigated [208]. RAIRS spectra of several alkenes have been compared with transmission infrared spectra of the alkenes on a Pt/SiO₂ catalyst [207].

Cyclohexane adsorption on Pd(110) [150] and on Pt(100) [152] has also been studied. In an investigation of cyclohexane adsorption on Pt(111) [151],
a broad shifted band was observed resulting from the interaction between the CH bonds of the cyclohexane and the metal surface, the so called ‘soft band’. In that study, RAIRS spectra were also reported of \( n \)-hexane, 2,2-dimethylpropane and cyclopentane in order to investigate the occurrence of the soft C-H stretching band observed for cyclohexane. Soft bands were indeed observed for these molecules, and it was noted that the soft bands were very weak and broad, and so more difficult to observe than using EELS, although the integrated area under the broad soft band relative to that under the sharp bands observed in the same spectrum showed the soft band to be the most intense band in the spectrum, as with EELS. Adsorption of but-1-ene and isobutene on Ru(0001) has been investigated using RAIRS [209], as well as adsorption of \textit{trans–}but-2-ene [210]. Chesters has recently published two general articles including RAIRS spectra [211, 212]. Sheppard has published a comprehensive review of vibrational spectroscopic studies of species derived from adsorbed hydrocarbons on metal single crystal surfaces [213].

4.6 Previous surface studies

Cyclopentene

Results from previous observation of cyclopentene adsorption on single crystals was discussed and summarised in the previous Chapter. A model of cyclopentene behaviour on Pt(111) was shown in Figure 3–20. However, no vibrational bands could be observed in the CH deformation region using DRIFTS or transmission infrared spectroscopy due to strong absorption by the silica support below 1400 or 1300 cm\(^{-1}\), respectively. Consequently, study in that Chapter was concerned solely with CH stretching vibrations which were easily observed. In RAIRS there is no such problem, and the limiting factor at low wavenumber is the detector cut-off at around 850 cm\(^{-1}\). Hence the RAIRS spectra provide a vibrational spectrum across a wide region and
can be analysed in comparison with EELS spectra across a similar spectral range. The vibrational data discussed previously (mainly EELS relating to the CH stretching region of the infrared spectrum) is described in more detail here, with particular relevance to the RAIRS study undertaken.

Avery's studies of cyclopentene adsorption on Pt(111) showed a submonolayer spectrum recorded at 90K, and a saturation coverage spectrum also recorded at 90K, after heating a previously saturated surface to 180K to evaporate excess multilayer [136]. The conspicuous bands observed for a submonolayer, saturated and a multilayer covered surface are summarised in Table 4–2. All Avery's EELS spectra were recorded in the specular direction. The infrared frequencies from some vibrational studies of cyclopentene are listed, with the appropriate symmetry species under C\textsubscript{2v} symmetry, in Table 4–3 for comparison. The bands are listed under the assignment of [160], with any differences indicated. The vibrational spectrum of cyclopentene is normally interpreted in terms of C\textsubscript{2v} symmetry [160], although it is known to be non-planar (C\textsubscript{s} symmetry). However, slight bending of the molecule away from planar results in only a small perturbation of the C\textsubscript{2v} selection rules. Hence there are 33 fundamental vibrations, but those of A\textsubscript{2} symmetry are not infrared active.

The \(\pi\text{-}(\text{CH})\) vibration at 3085cm\textsuperscript{-1}, \(\nu\text{ (C=C)}\) at 1630cm\textsuperscript{-1} and strong cis-\(\pi\text{ (=CH)}\) out of plane wagging mode at 700cm\textsuperscript{-1} are all attenuated in the sub-monolayer and monolayer spectra. This was interpreted to indicate that bonding to the surface occurred by considerable rehybridisation of the alkene carbon atoms, indicating that cyclopentene is bonded to Pt(111) in an \(\eta_2\text{-di-}\sigma\) form rather than \textit{via} \(\pi\) bonding. This interpretation was supported by the observation that the two bands at 2890 and 2970cm\textsuperscript{-1} are about 40cm\textsuperscript{-1} higher than expected for an unstrained methylene (-CH\textsubscript{2}-) group [136] and are more consistent with the slightly strained cyclopentane ring, where \(\nu\text{ (CH\textsubscript{2})}\) is 2865cm\textsuperscript{-1} and \(\nu\text{as (CH\textsubscript{2})}\) is 2955cm\textsuperscript{-1} [167]. The feature at 2695cm\textsuperscript{-1}, apparent at low coverage, which shifted to 2750cm\textsuperscript{-1} at saturation was ascribed to a soft band after Demuth [146].

199
Table 4–2: Summary of EELS vibrational frequencies of cyclopentene from previous studies, from [136].

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\tilde{\nu}$/cm$^{-1}$</th>
<th>sub-monolayer (93K) *</th>
<th>multilayer 90K</th>
<th>saturated surface 250K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (CH)</td>
<td></td>
<td>3080(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$ (CH$_2$)</td>
<td>2970</td>
<td>2975(m)</td>
<td>2970</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (CH) soft</td>
<td>2695</td>
<td></td>
<td></td>
<td>2695-2750</td>
</tr>
<tr>
<td>$\nu$ (C=C)</td>
<td></td>
<td>1630(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$ (CH$_2$)</td>
<td>1460</td>
<td>1470(m)</td>
<td>1460</td>
<td></td>
</tr>
<tr>
<td>$\rho$$_w$ (CH$_2$)</td>
<td>1295</td>
<td>1310(w)</td>
<td>1295</td>
<td></td>
</tr>
<tr>
<td>$\rho$$_w$ (CH$_2$)</td>
<td>1230</td>
<td>1230(w)</td>
<td>1230</td>
<td></td>
</tr>
<tr>
<td>$\nu$_as (CC)</td>
<td>1090</td>
<td>1050(m)</td>
<td>1090</td>
<td></td>
</tr>
<tr>
<td>$\nu$_s (CC)</td>
<td>880</td>
<td>910(m)</td>
<td>880(vs)</td>
<td></td>
</tr>
<tr>
<td>$\pi$ (CH)</td>
<td></td>
<td>705(s)</td>
<td>720(w)</td>
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</tr>
<tr>
<td>$\delta$ (CCC)</td>
<td>600</td>
<td>620(m)</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (Pt-c-C$_5$H$_8$)</td>
<td>450</td>
<td></td>
<td></td>
<td>450</td>
</tr>
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</table>

* peak positions not quoted, but estimated from the spectrum presented.
<table>
<thead>
<tr>
<th>Mode</th>
<th>Assignment</th>
<th>ν /cm⁻¹</th>
<th>IR</th>
<th>IR</th>
<th>IR</th>
<th>IR</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>CH sym. str.</td>
<td>A₁</td>
<td>3078(s)</td>
<td>3057</td>
<td>3066(s) [163]</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>CH antisym. str.</td>
<td>B₁</td>
<td>3068(s)</td>
<td>3050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>α-CH₂ antisym. str. (i.p.)</td>
<td>B₂</td>
<td>2965(s)</td>
<td>2955</td>
<td>2958(vs) [163]</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>β-CH₂ antisym. str.</td>
<td>B₂</td>
<td>2933(s)</td>
<td>2925</td>
<td>2902(vs) [163]</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>β-CH₂ sym. str.</td>
<td>A₁</td>
<td>2903(s)</td>
<td>2900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>α-CH₂ sym. str. (o.p.)</td>
<td>B₁</td>
<td>2873(s)</td>
<td>2865</td>
<td>2927(vs) [163]</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>α-CH₂ sym. str. (i.p)</td>
<td>A₁</td>
<td>2860(s)</td>
<td>2849</td>
<td>2852(vs) [163]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C=O str.</td>
<td>A₁</td>
<td>1623(m)</td>
<td>1610</td>
<td>1619</td>
<td>1613(m)</td>
</tr>
<tr>
<td>5</td>
<td>β-CH₂ def.</td>
<td>A₁</td>
<td>1471(vw)</td>
<td>1463</td>
<td>1465</td>
<td>1464(m)</td>
</tr>
<tr>
<td>6</td>
<td>α-CH₂ def. (i.p.)</td>
<td>A₁</td>
<td>1445(m)</td>
<td>1443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>α-CH₂ def. (o.p.)</td>
<td>B₁</td>
<td>1438(vw)</td>
<td>1437</td>
<td>1445</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Δ-CH bend (o.p.)</td>
<td>B₁</td>
<td>1353(m)</td>
<td>1348</td>
<td>1351</td>
<td>1350(s)</td>
</tr>
<tr>
<td>7</td>
<td>α-CH₂ wag (i.p.)</td>
<td>A₁</td>
<td>1290(m)</td>
<td>1293</td>
<td>1297</td>
<td>1296(s)</td>
</tr>
<tr>
<td>22</td>
<td>α-CH₂ wag (o.p.)</td>
<td>B₁</td>
<td>1268(m)</td>
<td>1275</td>
<td>1282</td>
<td>1277(m)</td>
</tr>
<tr>
<td>29</td>
<td>α-CH₂ twist (i.p.)</td>
<td>B₂</td>
<td>1207(m)</td>
<td></td>
<td>1206(B₁)</td>
<td>1206(mw)b</td>
</tr>
<tr>
<td>23</td>
<td>β-CH₂ wag</td>
<td>B₁</td>
<td>1128(w)</td>
<td>1128</td>
<td>1127(B₂)</td>
<td>1128(w)</td>
</tr>
<tr>
<td>8</td>
<td>Δ-CH bend i.p.</td>
<td>A₁</td>
<td>1101(w)</td>
<td>1100</td>
<td>1107a</td>
<td>1100(w)</td>
</tr>
<tr>
<td>30</td>
<td>α-CH₂ rock (i.p.)</td>
<td>B₂</td>
<td>1047(s)</td>
<td>1047</td>
<td>1043(B₁)</td>
<td>1045(s)</td>
</tr>
<tr>
<td>24</td>
<td>ring mode</td>
<td>B₁</td>
<td>1037(w)</td>
<td>1025</td>
<td>1020(B₂)</td>
<td>1025(w)</td>
</tr>
<tr>
<td>9</td>
<td>ring mode</td>
<td>A₁</td>
<td>962(w)</td>
<td>963</td>
<td>965</td>
<td>965(m)</td>
</tr>
<tr>
<td>25</td>
<td>ring mode</td>
<td>B₁</td>
<td>933</td>
<td>937a</td>
<td>934</td>
<td>934(w)</td>
</tr>
<tr>
<td>10</td>
<td>ring mode</td>
<td>A₁</td>
<td>900(m)</td>
<td>878</td>
<td>904</td>
<td>906(vs)</td>
</tr>
<tr>
<td>31</td>
<td>γ-CH bend (i.p.)</td>
<td>B₂</td>
<td>695</td>
<td>697</td>
<td>698(A₂)</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>ring mode</td>
<td>B₁</td>
<td>695(s)</td>
<td>697</td>
<td></td>
<td>700</td>
</tr>
<tr>
<td>11</td>
<td>ring mode</td>
<td>A₁</td>
<td>608(w)</td>
<td>604</td>
<td>603</td>
<td>605(m)</td>
</tr>
<tr>
<td>32</td>
<td>β-CH₂ rock</td>
<td>B₂</td>
<td>593(m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>ring puckering</td>
<td>B₂</td>
<td>127a</td>
<td>162</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Raman frequency
b Assigned as ν₁,3
c Assigned as ν₁,6

Δ = in plane, γ = out of plane, i.p. = in phase, o.p. = out of phase.
Following annealing the adsorbed cyclopentene to $250 \rightarrow 300\text{K}$, the EELS spectrum obtained was simpler than those previously described. The spectrum shows evidence of unsaturated CH vibrations at $3060\text{cm}^{-1}$, and the spectrum was assigned to an adsorbed pentahaptocyclopentadienyl $\eta_5$-C$_5$H$_5$($\eta_5$-Cp) species from comparison with the infrared spectra of ferrocene FeCp$_2$ [166] and the planar cyclopentadienylide anion, Cp$^-$ [165], as shown in Table 4-4, with the appropriate symmetry species under $D_{5d}$ symmetry (Ferrocene has $D_{5h}$ symmetry in the eclipsed form and $D_{5d}$ symmetry in the staggered form). However, with the low resolution of EELS, bands from the CH vibrations at the point of attachment of the $\eta_2$ ring to the surface could not be resolved from methylene vibrations.

Heating this species in a molecular beam of D$_2$ at $460\text{K}$ for 60s resulted in exchange of the hydrogen atoms giving shifted EELS bands at 2280 and $605\text{cm}^{-1}$, as listed under the column headed D$_2$ in Table 4-4. The isotopic shifts of 1.32 and 1.39 of the 3060 and 840$\text{cm}^{-1}$ bands confirm that these bands are dominated by motion of the H atoms. Further heating leads to a loss in intensity of the peaks and at $700\text{K}$, very weak bands at 840, 1150 and 3070$\text{cm}^{-1}$ were observed, and beyond this temperature, an essentially clean spectrum was observed.

Avery has also studied the adsorption and reactivity of 1-3 cyclopentadiene on Pt(111) using EELS [215]. On heating a saturated layer of c-C$_5$H$_6$ to $200\text{K}$, a spectrum arising from a mixture of $\eta^5$-Cp and $\eta^2$-di-$\sigma$-c-C$_5$H$_8$ was recorded.

Cyclopentene (and cyclopentadiene) adsorption has been studied on Rh (111) using Angle Resolved UV Photoelectron Spectroscopy (ARUPS) along with LEED and TDS [216]. Near Edge X-ray Absorption Fine Structure (NEXAFS) for cyclopentene has been measured, and seems to indicate cyclopentene to be adsorbed on Pt(111) as a $\pi$ bonded species, in contrast to Avery's EELS studies described above [217]. The surface chemistry of cyclopentene on Rh(111) was found to be quite different from that on Pt(111). On Pt(111), the cyclopentene monolayer dehydrogenates to C$_5$H$_5$ at $250 \rightarrow$
Table 4-4: Vibrational frequencies and assignments of the cyclopentadienyl species, C₅H₅ (Cp).

<table>
<thead>
<tr>
<th>Mode</th>
<th>EELS [136]</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D₂ 370K</td>
<td>K⁺Cp⁻ 460K [165]</td>
</tr>
<tr>
<td></td>
<td>FeCp₂ [166]</td>
<td></td>
</tr>
<tr>
<td>ν(CH) A₂ᵣ</td>
<td>3060</td>
<td>3096ᵃ</td>
</tr>
<tr>
<td></td>
<td>2280</td>
<td>3085(s)</td>
</tr>
<tr>
<td>ν(CH) A₁ᵣ</td>
<td>2990ᵇ</td>
<td>3039</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3075(s)</td>
</tr>
<tr>
<td>νₐs(CC) E₁ᵣ</td>
<td>1455</td>
<td>1411(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1245</td>
</tr>
<tr>
<td>νₛ(CC) A₂ᵣ</td>
<td></td>
<td>1108(s)</td>
</tr>
<tr>
<td>δ(CH) E₁ᵣ</td>
<td>1033</td>
<td>1002(s)</td>
</tr>
<tr>
<td>π(CH) A₂ᵣ</td>
<td>840</td>
<td>605</td>
</tr>
<tr>
<td></td>
<td>710</td>
<td>811(s)</td>
</tr>
<tr>
<td></td>
<td>E₁ᵣ</td>
<td>834(w)</td>
</tr>
<tr>
<td>ring tilt</td>
<td>E₁ᵣ</td>
<td>492(s)</td>
</tr>
<tr>
<td>νₐs(MCp₂) A₂ᵣ</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>νₛ(MCp₂)</td>
<td></td>
<td>303</td>
</tr>
<tr>
<td>δ(MCp₂) E₁ᵣ</td>
<td></td>
<td>170(m)</td>
</tr>
</tbody>
</table>

ᵃ Raman active mode
ᵇ This band was originally reported at 3010 cm⁻¹ and adjusted after further study
300K, and on Rh(111) it dehydrogenates to a species of $\text{C}_5\text{H}_6$ stoichiometry above 190K. $\eta^5\text{-C}_5\text{H}_5$ is only formed on Rh(111) following adsorption at 290K.

**Cyclopentane**

The specular EELS spectra recorded by Avery for cyclopentane adsorbed on Pt(111) are described in detail below [139]. Spectra were recorded at 90K showing multilayer adsorption, and then after subsequent annealing. The band positions and their assignment for both spectra are listed in Table 4–5, with corresponding symmetry species of gas phase cyclopentane, $D_{5h}$. In liquid cyclopentane, $D_{5h}$ symmetry approximately applies although modest ring puckering exists. However, the hydrogen atoms remain essentially eclipsed.

The spectrum observed after annealing to 180K could also be produced, although more weakly, from submonolayer exposure at 90K. The very strong soft CH stretching band extending from 2320–2880 cm$^{-1}$ dominates the 180K spectrum, peaking at 2690 cm$^{-1}$. Heating to 200K resulted in the concomitant molecular cyclopentane desorption and partial dehydrogenation to $\eta^2\text{-di-}\sigma\text{-c-C}_5\text{H}_8$, with an EELS spectrum similar to that observed following cyclopentene adsorption observed [135, 136]. Further annealing, to 263K produced an EELS spectrum characteristic of $\eta^5\text{-Cp}$.

The only reported RAIRS spectrum of cyclopentane adsorption on Pt(111), recorded at 130 $\rightarrow$ 150K shows absorption bands at around 2960, 2920 and 2880 cm$^{-1}$ with a broad soft CH band extending between 2400–2850 cm$^{-1}$ [151]. No vibrations in any other region of the spectrum were reported or discussed, as the study was primarily concerned with observing soft C-H bands.

EELS has also been used to study cyclopentane adsorption on Ru(001) [153]. Two specular EELS spectra were shown, of monolayer coverage obtained by annealing a multilayer to 170K, and following heating to 200K where the spectrum, was ascribed to adsorbed cyclopentene. Characteristic
Table 4–5: Summary of literature vibrational frequencies of cyclopentane.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\nu$/cm$^{-1}$</th>
<th>IR gas[168]</th>
<th>IR liquid[168]</th>
<th>IR liquid[167]</th>
<th>RAIRS$^a$ [151]</th>
<th>EELS Pt(111) [139]</th>
<th>EELS Ru(001) [153]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(CH$_2$)</td>
<td>$A''_2$</td>
<td>2966</td>
<td>2960(vs)</td>
<td>2960(s)</td>
<td>2960(s)</td>
<td>2969</td>
<td>2935</td>
</tr>
<tr>
<td>$\nu$(CH$_2$)</td>
<td>$E'_1$</td>
<td>2878</td>
<td>2890(vs)</td>
<td>2866(vs)</td>
<td>sh</td>
<td>2880-</td>
<td>2850-</td>
</tr>
<tr>
<td>$\nu$(CH soft)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2320(vs)</td>
<td>2400</td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_1$</td>
<td>1462</td>
<td>1456(s)</td>
<td>1450(vs)</td>
<td>1455(m)</td>
<td>1450(m)</td>
<td>1460</td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_1$</td>
<td>1312</td>
<td>1316(w)</td>
<td>1315(s)</td>
<td>1310(m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_2$</td>
<td>1250(w)</td>
<td></td>
<td></td>
<td></td>
<td>1290</td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$A'_2$</td>
<td>1260(w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_1$</td>
<td>1210(w)</td>
<td>1230(m)$^b$</td>
<td>1230(m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_2$</td>
<td>1030(vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_1$</td>
<td>970(w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$(C-C)</td>
<td>$E'_1$</td>
<td>897</td>
<td>896(s)</td>
<td>896(s)</td>
<td>895(m)</td>
<td></td>
<td>903</td>
</tr>
<tr>
<td>$\nu$(C-C)</td>
<td>$E'_2$</td>
<td></td>
<td>860(sh)</td>
<td></td>
<td></td>
<td>860(m)</td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E''_2$</td>
<td>775(vw)</td>
<td></td>
<td></td>
<td></td>
<td>770(m)</td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>$E'_{2}$</td>
<td>545</td>
<td>546(w)</td>
<td>545(m)</td>
<td>550(m)</td>
<td>540(s)</td>
<td>524$^c$</td>
</tr>
<tr>
<td>$\nu$(Pt-C$<em>5$H$</em>{10}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>270(vs)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Approximate frequencies measured from Figure 4 in [151](2300–3100 cm$^{-1}$)

$^b$ Assigned as possibly $\rho$(CH$_2$)$_2$ $A'_2$ and $E'_2$ and $\rho$(CH$_2$)$_2$ $B'_1$ and $E''_2$ modes

$^c$ Presumed to also contain some intensity from the M-CO stretching vibration of residual CO adsorbed from the gas phase

205
C-H stretching vibrations were observed at 2855cm\(^{-1}\) (-C-H) and 3057cm\(^{-1}\) (=C-H) and a strong ring deformation was observed at 758cm\(^{-1}\).

### 4.7 Experimental

The Reflection Absorption Infrared (RAIRS) experiments described in this Chapter were carried out using the apparatus described below. Adsorption was studied on a Pt(111) single crystal and the details of its mounting and preparation are described later. As mentioned in Section 1.4, the crystal must be handled in an ultra high vacuum environment in order to prepare and maintain a clean surface for adsorption. Firstly, the vacuum system and associated gas handling facilities are described.

#### 4.7.1 Vacuum System

The crystal was held within a stainless steel ultra high vacuum chamber constructed by Cryogenic and Vacuum Technology (CVT), Milton Keynes. This is illustrated schematically in Figures 4–8 and 4–9.

The UHV system consists of a main chamber, pumped by an oil diffusion pump (Edwards EO4K, pumping speed 600 ls\(^{-1}\)) backed by a rotary pump (Edwards E2M5 Double Stage). The base pressure attainable in the main chamber, pumping from atmospheric pressure was in the 10\(^{-7}\) mbar range within a matter of minutes. An ion pump was also connected to the main chamber (Leybold Heraeus IZ50), acting as an auxilliary pump to the diffusion pump. The base pressure of the system could be lowered by enclosing the entire UHV system above the level of the table within a removable oven. The enclosed system could then be heated (normally to 393K), using thermostatically controlled heating elements, typically for 24–48 hours. This allowed water and other volatile species adsorbed on the inner walls of the system to be desorbed and pumped away. The effect of this was to improve
Figure 4-8: Illustration of the UHV system and IR Spectrometer.

- Electrical and thermocouple ceramic feedthroughs
- Manipulator
- Evacuable Optics Housing
- Digilab FM40 Spectrometer
- Vibration Free Table
- KBr Lens
detector
- Main UHV Chamber
- TSP
- Ion pump
- to gas handling line
to glass vacuum line
- Diffusion pumps
Figure 4-9: Schematic illustration of the layout of the UHV system.

KEY
V=Valve
B=Baratron
P=Pirani
FT=Foreline Trap
TSP=Titanium Sublimation Pump
MCT=Pumping to Detector
Ion=Ion Gauge
the ultimate vacuum achievable from the $10^{-7}$ mbar range to a pressure in the $10^{-10}$ mbar range. At the end of bakeout, the system was allowed to cool with the oven still in place for several hours, pumping into the ion pump with the diffusion pump isolated from the main chamber to prevent any possible backstreaming of water or oil into the main chamber. This procedure allowed the system to cool at a controlled rate and minimised any thermal stress on ceramics and other fragile components. Following cooling, the oven was removed and the liquid nitrogen trap above the diffusion pump was filled prior to opening the valve to the main chamber. All filaments within the chamber were outgassed while the system was still hot to minimise any possible subsequent pressure limiting pressure bursts. The system was then left for several hours to cool to room temperature and reach its base pressure.

A further pump, a liquid nitrogen cooled Titanium Sublimation Pump (TSP) (CVT TSP 1/70), situated between the main chamber and the diffusion pump, was used to supplement the diffusion pump and for rapid pumping prior to an experiment. When it was not possible to keep the liquid nitrogen trap filled, the main chamber was isolated from the diffusion pump and left pumping via the ion pump. This was capable of maintaining a pressure of $\sim 5 \times 10^{-9}$ mbar. Following this, the liquid nitrogen trap was filled prior to reopening the valve to the diffusion pump.

The system had to be baked out in the manner described above following every time it was let up to atmospheric pressure, in order to attain the ultimate base pressure in the $10^{-10}$ mbar range.

4.7.2 Crystal Mounting and Preparation

The Pt(111) single crystal used in this study was supplied by Goodfellow Metals. It was a circular disc, of 14mm diameter and 2mm thickness, and of 5N purity. Two spark eroded grooves were made on opposite sides of the edge of the crystal, which was mounted onto a copper rod using 0.5mm
tungsten wires passing through the grooves. These formed a loop which was fixed to the copper rod by passing round two screws above and below the crystal. This acted as a support as well as for heating the crystal. Heating was achieved by passing a DC current along copper wires connected to the tungsten wire thus resistively heating the crystal to temperatures above 873K. The mounting of the crystal is shown schematically in Figure 4-10.

The crystal and loop of tungsten wire were kept electrically insulated from the copper rod using UHV compatible ceramics. The crystal could also be cooled to $\sim 123K$ as the copper rod was in thermal contact with a liquid nitrogen reservoir. This was filled with liquid nitrogen in order to cool the crystal and to assist in rapid cooling after flashing prior to an experiment. The temperature of the crystal was measured using a chromel-alumel thermocouple inserted into a spark eroded hole at the top edge of the crystal. The two copper heating wires and the thermocouple wires were fed through 4-bore ceramics to connections leading through ceramic feedthroughs to the atmosphere.

The copper rod which the crystal was mounted on was attached to the end of a stainless steel rod, and the entire assembly could be manipulated to limited degrees to move the crystal within the UHV system in three dimensions. It could be moved vertically, and translated along both horizontal axes, calibrated accurately using a vernier scale. The manipulator assembly was attached to the main chamber via a differentially pumped rotary head assembly such that the volume around the the rotatable head (between UHV and atmospheric pressure) could be differentially pumped.

Movement of the crystal within the main chamber was necessary for cleaning and characterisation of the crystal surface. 'In vacuo' cleaning involved argon ion bombardment using the attached argon ion gun (typical ion current 6$\mu$Amps and 2keV energy). However, this was not found to be sufficient to achieve a clean surface, and cycles of heating under $5 \times 10^{-6}$ mbar of O$_2$ at 896K followed by annealing under vacuum at the same tem-
Figure 4-10: Illustration of the crystal mounting.
perature for many hours were necessary. This cleaning method is similar to
those previously reported [218].

Surface cleanliness was monitored using Auger Electron Spectroscopy
(AES) and Low Energy Electron Diffraction (LEED) Combined LEED/
Auger optics (VG Model 640 LEED/Auger Optics) were used to view LEED
patterns or to record Auger Electron Spectra. Their use is described briefly
below.

The optics consist of a concave phosphor screen and four concentric
parabolic mesh grids centered on the crystal which is positioned to face
the optics. This is illustrated schematically in Figure 4–11. The crystal
faces a hot (thoria coated tantalum) filament electron gun which produces
electrons that impinge on the crystal at normal incidence.

In LEED mode, the diffraction pattern is obtained at low electron beam
energy, typically <100eV. It is obtained on the phosphor screen and viewed
through the viewport in the main chamber sited parallel to the LEED/Auger
optics. The grid nearest the sample (G4) is set at earth potential, as is
the crystal. This ensures that electrons diffracted from the crystal travel
through a field free region to the other grids, thus maintaining their radial
geometry. A retarding voltage is applied to grid G2 to ensure that only elas-
tically scattered electrons reach the screen, and those with lower energy are
repelled. Electrons are then accelerated to the phosphor screen by applying
5kV to the screen. The typical beam current used was 2–3 μAmps.

For Auger operation, the optics were reset to energy analyse the sec-
ondary electrons produced from the crystal. The phosphor screen was used
as an electron collector and was biased with a small positive voltage. A
programmed retarding voltage is supplied to grids G3 and G3a, and only
electrons with sufficient energy to overcome this voltage reach the screen.

A conventional Auger spectrum is obtained by double differentiation of
the collected current as a function of retarding voltage (i.e. electron en-
ergy). This is done electronically using the lock-in amplifier. In principle, a
Figure 4-11: Schematic diagram of the operation of the LEED/Auger optics.
small sinusoidal voltage is added to the retarding voltage and the resulting AC component of the collected current is detected by the lock-in amplifier operating at twice the modulation frequency. The output from the lock in amplifier is plotted as a function of the retarding voltage to give a conventional Auger spectrum which is output to a chart recorder. Typically, 2.9 keV was used as the electron gun voltage.

In this study, LEED and Auger were used only to confirm the periodicity and cleanness of the surface prior to infrared experiments. No attempt was made to quantify the Auger spectra or to analyse spot intensities in the LEED patterns observed.

The main surface contaminants were found using AES to be carbon (273 eV) and sulphur (152 eV). The Auger peaks were assigned by comparison with reference spectra [219]. The region 350–100 eV was normally scanned in an Auger spectrum since platinum has minor peaks at 248, 233, 165 and 156 eV. The main Auger peak for platinum occurs at 63 eV, but it was not possible to detect this peak due to the large elastically scattered electron signal in this region. Oxygen has an Auger peak at 510 eV and this was also monitored, particularly following heating under oxygen. Typical Auger electron spectra recorded for a contaminated and a clean surface are shown in Figure 4–12. The clean Pt(111) surface showed a sharp (1×1) LEED pattern.

It was found that the most effective way of checking the surface order and purity of the crystal prior to an infrared experiment was to adsorb CO to saturation coverage, and to use the frequency and half width of the observed band due to linearly adsorbed CO to determine the condition of the surface. An example of a RAIRS spectrum of CO on Pt(111) is shown in Figure 4–13. The strong band at 2087 cm⁻¹ is due to linearly bonded CO, and the weak peak at 1857 cm⁻¹ is due to bridge bonded CO.
Figure 4-12: Examples of Auger Spectra recorded for (a) a contaminated surface, and (b) a clean surface
4.7.3 Infrared Setup

The experimental setup for a reflection experiment involved translation of the crystal from the main chamber to the small high pressure infrared cell situated immediately below. The sample holder seats on two 'O' rings to seal. The volume enclosed between these 'O' rings can be differentially pumped when the crystal is isolated in the high pressure cell, allowing high pressures of gases to be used in the infrared cell whilst maintaining the main chamber at ultra high vacuum.

The location of the crystal in the infrared cell is shown in Figure 4–14. The infrared cell is situated in line with the infrared beam, which is taken outwith the optical bench of the Digilab FTS-40 Infrared Spectrometer. For DRIFTS and transmission experiments, the infrared beam path was as shown in Figure 3–11. For RAIRS operation, the parabolic mirror used to direct the beam through the sample compartment was removed and replaced with a plane mirror to direct the beam towards the crystal.
Figure 4–14: Illustration of the position of the crystal in the high pressure cell.
The direction of the beam from the spectrometer through evacuable housing to the infrared cell is shown in Figure 4–15. During an experiment, the path of the beam is kept evacuated using a rotary pump to minimise cancellation features due to atmospheric water and CO₂. On passing between the optical bench and the infrared cell, the beam passes through a KBr lens, positioned to focus it onto the crystal. The detector is positioned on the other side of the infrared cell, and the associated optics are connected through evacuable housing. The infrared beam enters and leaves the infrared cell by passing through two circular 25 × 5mm circular KBr windows. These are mounted on a differentially pumped 'O' ring seal. The geometry of the infrared cell and the beam is shown in Figure 4–16. This shows how the infrared beam is incident on the crystal surface at almost grazing incidence, 5°.

The optics were set up for a reflection experiment by first lowering the crystal into the infrared cell. The position of the plane mirror, KBr lens, detector mirrors and the detector were all then adjusted in turn to optimise the signal reflected from the crystal. This was performed by continuously monitoring the intensity of the zero retardation peak of the interferogram. The plane mirror and the KBr lens were then fixed securely, the spectrometer optical bench closed and evacuated. The transfer optics and detector optics housing were also evacuated at this stage, to around 10⁻³ mbar. The detector dewar itself was evacuated for several days prior to an experiment, using the small diffusion pump, via valve (33). This was in order to remove any water present to prevent ice formation on the cooled element of the detector which introduces broad bands at ~3300cm⁻¹ in the recorded spectra.

4.7.4 Gas Handling

Gases used for crystal cleaning and for adsorption were prepared using the gas handling section of the system below the table top. This was pumped separately from the main UHV chamber using a smaller oil diffusion pump.
to the crystal.

Figure 4-15: Illustration of the infrared beam path from the spectrometer.
(Edwards EO2K, pumping speed 150 ls$^{-1}$) backed by a double stage rotary pump (Edwards E2M2). Gases were admitted to the main chamber via valve 35 (V35 in Figure 4–9). Gases were stored at high pressure in lecture bottles attached to the gas handling manifold. The gas handling line was normally pumped to rotary pump vacuum, and was pumped using the diffusion pump prior to admission of any gas. The pressure in this region was monitored using a Penning gauge (Penningvac PM410). A volume of gas was enclosed between valves V34 and V35 and was admitted to the main chamber from this reservoir. The rate of flow of gas into the chamber was controlled using the variable leak valve V35.

The pressure in the main chamber was measured using an ion gauge (Leybold Heraeus Ionivac 1M510). All pressures in rotary pumped volumes, and

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$^2$Valves referred to in this section are those labelled in Figure 4–9
the diffusion pump backing pressures were measured using Pirani gauges (Leybold Heraeus Thermovac TM2105 and TM22052). The Pirani gauges are shown by P1–P4 in Figure 4–9.

The hydrocarbons, all liquids at room temperature and pressure were stored in glass vessels sealed with a 'Young's' greaseless vacuum tap. These could be attached to the glass line situated below the table top, and connected via a closeable valve to the volume between valves 34 and 35. The purity and suppliers of all gases and chemicals used are listed with those from previous Chapters in Appendix A.

4.8 Results

The operation of the infrared spectrometer was as described in Section 3.8, with the optics set up for RAIRS. As for DRIFTS or transmission, an interferogram such as that in Figure 3–17 was recorded. This was then computed to generate a single beam spectrum, an example of which is shown in Figure 4–17. The RAIRS single beam spectrum shows a different profile to the DRIFTS or transmission single beam spectra. The overall detector response in a RAIRS experiment is at a similar level to that obtained using DRIFTS, and both are considerably less than in transmission mode. The low frequency detection limit is that of the detector (~850cm⁻¹), as there is no support cut-off as seen for both DRIFTS and transmission.

As before, reflection spectra of the adsorbed hydrocarbon were generated by recording a background spectrum of the clean crystal, and recording subsequent single beam spectra following dosing an adsorbate without altering the position of the crystal. Each spectrum of the adsorbate on the crystal was then ratioed against the background spectrum to produce an absorbance spectrum. A considerably larger number of scans had, however, to be recorded in order to achieve a satisfactory signal to noise level. This was typically several hundred or thousands of scans, and in this study 5000
scans were necessary, with a total acquisition time of 44 minutes for each spectrum. All RAIRS spectra were recorded under flowing hydrocarbon, rather than after a calibrated exposure.

Again for ease of reference, all RAIRS spectra are grouped together at the end of this Chapter. Spectra are plotted in absorbance units throughout, and are not baseline corrected unless otherwise stated.

4.8.1 Cyclopentene adsorption at low temperature

A series of RAIRS spectra was recorded during adsorption of cyclopentene on Pt(111) at 173K, and during subsequent heating. Figure 4–22 shows the CH stretching region, $\nu$ (CH) from 3150 $\rightarrow$ 2750cm$^{-1}$, recorded under $1 \times 10^{-9}$ mbar flowing cyclopentene at 173K. The spectrum shows some weak CH stretching vibrations, and some very weak peaks were apparent elsewhere in the spectrum, at 1044, 1203, 1294 and 1350cm$^{-1}$, although this part of
the spectrum is not reproduced here. The first spectrum was recorded at very low (sub-monolayer) coverage. The positions of the bands observed are listed in Table 4–6 with those from multilayer adsorption, discussed below, following exposure to higher pressures of cyclopentene, with the proposed band assignments.

The spectrum recorded under $5 \times 10^{-9}$ mbar of cyclopentene is shown in Figures 4–23 and 4–24, recorded with the crystal temperature still at 173K. This spectrum shows many strong absorption bands, notably in the CH stretching region of the spectrum, and also one at 1044 cm$^{-1}$. The complete (baseline corrected) spectrum is also plotted in Figure 4–25. The position and relative intensities of these bands are listed in Table 4–6.

The spectrum recorded under $1 \times 10^{-8}$ mbar of flowing cyclopentene, resulted in further growth in intensity of the bands observed in the previous spectrum, showing that many layers of cyclopentene can be held on the surface. This is shown in the spectrum shown in Figures 4–26 and 4–27. The complete (baseline corrected) spectrum is shown in Figure 4–28, and shows more intense absorption bands than the previous spectrum. Following this, a series of spectra was recorded as the crystal was heated to increasing temperatures, in order to observe the behaviour at higher temperatures and investigate any potential formation of the cyclopentadienyl species, as observed in Avery's EELS study.

The spectrum recorded at 223K is shown in Figures 4–29 and 4–30. These Figures show a general decrease in intensity of all bands. The baseline slopes steeply in the low wavenumber region, corresponding to the point in the single beam spectrum, Figure 4–17, where the detector response falls rapidly to zero. Heating to 273K resulted in the spectrum shown in Figure 4–31 [$\nu$(CH) region]. This spectrum shows a further decrease in intensity of the bands observed, with some small changes in the relative intensities, with the 2928 cm$^{-1}$ band coming up in relative intensity. Only very weak bands were visible in the remainder of the spectrum which is not shown. After heating the crystal to 293K, the spectrum shown in Figure 4–32 was
Table 4–6: Frequencies of submonolayer and multilayer coverage of cyclopentene on Pt(111), and proposed assignment.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>RAIRS Frequency [this study]</th>
<th>DRIFTS heated to 273K</th>
<th>EuroPt-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>submonolayer</td>
<td>multilayer</td>
<td></td>
</tr>
<tr>
<td>1  $\nu$ (CH)$_{sym}$</td>
<td>A$_1$</td>
<td>3055</td>
<td>3057(m)</td>
</tr>
<tr>
<td>18 $\nu$ (CH)$_{antisym}$</td>
<td>B$_1$</td>
<td>3048</td>
<td>3049(m)</td>
</tr>
<tr>
<td>27 $\alpha$-CH$_2$ antisym. str. (i.p.)</td>
<td>B$_2$</td>
<td>2944</td>
<td>2949(s)</td>
</tr>
<tr>
<td>28 $\beta$-CH$_2$ antisym. str.</td>
<td>B$_2$</td>
<td>2912</td>
<td>2917(m)</td>
</tr>
<tr>
<td>2 $\beta$-CH$_2$ sym. str.</td>
<td>A$_1$</td>
<td>2893</td>
<td>sh</td>
</tr>
<tr>
<td>19 $\alpha$-CH$_3$ sym. str. (o.p.)</td>
<td>B$_1$</td>
<td>2866(w)</td>
<td>2852</td>
</tr>
<tr>
<td>3 $\alpha$-CH$_2$ sym. str. (i.p)</td>
<td>A$_1$</td>
<td>2841</td>
<td>2847(s)</td>
</tr>
<tr>
<td>4 C=C str.</td>
<td>A$_1$</td>
<td>1613(w)</td>
<td></td>
</tr>
<tr>
<td>5 $\beta$-CH$_3$ def.</td>
<td>A$_1$</td>
<td>1464(w/m)</td>
<td></td>
</tr>
<tr>
<td>6 $\alpha$-CH$_3$ def (i.p.)</td>
<td>A$_1$</td>
<td>sh</td>
<td></td>
</tr>
<tr>
<td>20 $\alpha$-CH$_3$ def (o.p)</td>
<td>B$_1$</td>
<td>1439(w/m)</td>
<td></td>
</tr>
<tr>
<td>21 $\Delta$-CH bend (o.p.)</td>
<td>B$_1$</td>
<td>1350</td>
<td>1350(m)</td>
</tr>
<tr>
<td>7 $\alpha$-CH$_2$ wag (i.p.)</td>
<td>A$_1$</td>
<td>1294</td>
<td>1296(w/m)</td>
</tr>
<tr>
<td>22 $\alpha$-CH$_2$ wag (o.p.)</td>
<td>B$_1$</td>
<td>1277(w)</td>
<td></td>
</tr>
<tr>
<td>29 $\alpha$-CH$_2$ twist (i.p.)</td>
<td>B$_2$</td>
<td>1203</td>
<td>1206(w/m)</td>
</tr>
<tr>
<td>23 $\beta$-CH$_2$ wag</td>
<td>B$_1$</td>
<td>1130(w)</td>
<td></td>
</tr>
<tr>
<td>8 $\Delta$-CH bend i.p.</td>
<td>A$_1$</td>
<td>1103(w)</td>
<td></td>
</tr>
<tr>
<td>30 $\alpha$-CH$_2$ rock (i.p.)</td>
<td>B$_2$</td>
<td>1044</td>
<td>1044(vs)</td>
</tr>
<tr>
<td>24 ring mode</td>
<td>B$_1$</td>
<td>1026(w)</td>
<td></td>
</tr>
<tr>
<td>9 ring mode</td>
<td>A$_1$</td>
<td>965 (w/m)</td>
<td></td>
</tr>
<tr>
<td>10 ring mode</td>
<td>A$_1$</td>
<td>906(s)</td>
<td></td>
</tr>
</tbody>
</table>
recorded, and after heating to 423K the spectrum shown in Figure 4–33 was obtained. There is a shift in the baseline across the absorption bands in the \( \nu (\text{CH}) \) region which is apparent in the spectra recorded at 293K and 423K. The only bands evident in the \( \nu (\text{CH}) \) region are at 2921cm\(^{-1}\) and 2851cm\(^{-1}\). The final spectrum was recorded at 623K, and has a steeply sloping baseline. It is shown in Figure 4–34. This shows weak features in the \( \nu (\text{CH}) \) region, at 2967, 2926 and 2851cm\(^{-1}\).

**4.8.2 Blank Experiment**

In order to investigate whether the weak bands observed in the cyclopentene spectra recorded at high temperature (in the experiment described above) are due to real adsorbed species or to an artefact or miscancellation feature, some spectra were recorded of the clean crystal at a range of temperatures. This was done in the same way as the previous experiment, but without exposing the clean crystal to an adsorbate *i.e.* the clean crystal was heated under UHV conditions. The spectra were ratioed against a low temperature background spectrum as before. The \( \text{CH} \) stretching region of such a spectrum recorded at 273K is shown in Figure 4–35, and shows very weak peaks at 2920, 2876 and 2835cm\(^{-1}\). At 323K, the spectrum recorded, as shown in Figure 4–36 shows little evidence of any absorption bands. Further heating gave rise to very small peaks at 2927 and 2873/2853cm\(^{-1}\), as shown by the spectrum in Figure 4–37 recorded at 423K. The spectrum recorded at 623K, shown in Figure 4–38 shows weak peaks in the \( \text{CH} \) stretching region at 2920, 2872 and 2850cm\(^{-1}\).

**4.8.3 Cyclopentene adsorption at ambient temperature**

In an attempt to investigate the presence of the cyclopentadienyl species observed by Avery using EELS, adsorption of cyclopentene on Pt(111) at 303K was investigated. According to the model of cyclopentene chemistry on Pt(111) shown in Figure 3–20, associatively adsorbed cyclopentene at
low temperature undergoes dehydrogenation to the cyclopentadienyl species between 250 → 300K. Spectra recorded under increasing pressures of cyclopentene with the crystal temperature at 303K showed little evidence of adsorption observable with infrared spectroscopy. The $\nu$ (CH) region of such spectra recorded under increasing pressure of cyclopentene is shown in Figure 4–39.

### 4.8.4 Cyclopentane adsorption at low temperature

The spectrum of cyclopentane recorded at 135K under $5 \times 10^{-10}$ mbar, is shown in Figure 4–40 (CH stretching region). This spectrum, and all other cyclopentane RAIRS spectra described in this Section have been baseline corrected. This spectrum shows some strong absorption bands in the CH stretching region at 2953 and 2864 cm$^{-1}$ and a weaker shoulder at 2916 cm$^{-1}$, but there was little evidence of any bands in the deformation region. The low signal to noise ratio in this spectrum is due to the low surface coverage.

The spectrum recorded under $9 \times 10^{-10}$ mbar of cyclopentane at 133K is shown in Figure 4–41 (3050 → 2750 cm$^{-1}$). This shows a similar spectrum to that recorded at lower pressure but slightly more intense absorption bands with maxima at 2953 and 2864 cm$^{-1}$ as well as an indistinct shoulder to the 2953 cm$^{-1}$ band. Under $2 \times 10^{-9}$ mbar of cyclopentane at 131K, the spectrum obtained is shown in Figure 4–42. The CH stretching region again shows more intense bands with increasing exposure. The peaks observed were at 2951 and 2863 cm$^{-1}$ with a weak shoulder to the 2951 cm$^{-1}$ peak still apparent at 2915 cm$^{-1}$. The crystal was then exposed to $1 \times 10^{-8}$ mbar of flowing cyclopentane at 128K, and this resulted in the multilayer spectrum shown in Figures 4–43 and 4–44. Several absorption bands were observed in the deformation region, a medium intensity band at 1316 cm$^{-1}$, a strong band at 897 cm$^{-1}$ and a very intense band at 1452 cm$^{-1}$. Very strong peaks were observed in the CH stretching region at 2952 and 2864 cm$^{-1}$ with a prominent shoulder to the 2952 cm$^{-1}$ peak at 2914 cm$^{-1}$. The complete
Table 4-7: Position and proposed assignment of vibrations observed for cyclopentane on Pt(111).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Sub-monolayer</th>
<th>Multilayer</th>
<th>DRIFTS EuroPt-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (CH$<em>2$)$</em>{asym}$</td>
<td>A&quot;</td>
<td>2954</td>
<td>2952(vs)</td>
</tr>
<tr>
<td>$\nu$ (CH$_2$)</td>
<td>2916(sh)</td>
<td>2915(w/m)</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (CH$<em>2$)$</em>{sym}$</td>
<td>E'</td>
<td>2863</td>
<td>2864(m)</td>
</tr>
<tr>
<td>$\delta$ (CH$_2$)</td>
<td>E'</td>
<td>1452(w/m)</td>
<td></td>
</tr>
<tr>
<td>$\rho_w$ (CH$_2$)</td>
<td>E'</td>
<td>1315(w)</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (C-C) ring</td>
<td>E'</td>
<td>897(w)</td>
<td></td>
</tr>
</tbody>
</table>

The position and assignment of the observed bands is listed in Table 4-7, with the corresponding symmetry species of gas phase cyclopentane under D$_{5h}$ symmetry.

4.8.5 Methylcyclopentane adsorption at low temperature

As for cyclopentene and cyclopentane, a series of RAIRS spectra was recorded during adsorption of methylcyclopentane on Pt(111). The spectrum recorded at 118K under $5 \times 10^{-10}$ mbar of flowing methylcyclopentane is shown in Figure 4-46 [$\nu$ (CH) stretching region]. This spectrum, and other methylcyclopentane spectra shown in this Section have been baseline corrected. A reasonably strong band at 2953cm$^{-1}$ (with a slight shoulder visible at 2927cm$^{-1}$) and a weaker band at 2865cm$^{-1}$ are observable. Exposure of
the crystal to $1 \times 10^{-9}$ mbar of methylcyclopentane at 117K resulted in the spectrum shown in Figure 4-47. The CH stretching region shows stronger bands than the previous spectrum, with all peaks increasing in intensity and a distinct peak or shoulder apparent at 2909 cm$^{-1}$. In the CH deformation region, a weak absorption band is present at 1452 cm$^{-1}$, with no evidence of any other bands. This region of the spectrum is not shown, as the baseline was steeply curving and there were also some miscancellation features from gas phase water, and no hydrocarbon peaks other than the 1452 cm$^{-1}$ peak already mentioned were observed.

Increasing the methylcyclopentane pressure to $1 \times 10^{-8}$ mbar with the crystal temperature at 117K resulted in the spectrum shown in Figures 4-48 and 4-49. These spectra show strong absorption bands in the CH stretching region at 2955, 2945 (sh), 2934, 2918, 2906, 2876 and 2855 cm$^{-1}$. Several strong bands were also observed in the CH deformation region at 1460, 1451 (weak), 1445, 1373 and 1138 (weak) cm$^{-1}$. The complete spectrum is shown in Figure 4-50, showing the CH stretching vibrations to be the most intense. Under $5 \times 10^{-8}$ mbar of flowing methylcyclopentane, at 113K resulted in stronger absorption bands, as shown in Figures 4-51 and 4-52 as well as some additional bands. The complete spectrum is shown in Figure 4-53, again showing the $\nu$ (CH) bands to be the most intense. The crystal was then flashed to 403K leaving no absorption bands visible. The absorption bands observed for sub-monolayer and multilayer methylcyclopentane spectra ($\tilde{\nu}$ from the spectrum shown in Figure 4-53) are listed in Table 4-8 with the proposed assignment of the observed vibrations. The assignment was made on the basis of the cyclopentane results and the DRIFTS spectra described in the previous Chapter, as no detailed assignments of the vibrational spectrum of methylcyclopentane could be found.
Table 4–8: Assignment and frequency of methylcyclopentane vibrations.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\tilde{\nu}$/cm$^{-1}$</th>
<th>sub-monolayer</th>
<th>multi-layer</th>
<th>DRIFTS EuroPt-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (CH$<em>2$)$</em>{asym}$</td>
<td>2953</td>
<td>2957</td>
<td>2964(w/m)</td>
<td>2953</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2945</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2927</td>
<td>2934(sh)</td>
<td>2920</td>
</tr>
<tr>
<td>$\nu$ (CH$<em>3$)$</em>{sym}$</td>
<td>2907</td>
<td>2907(w/m)</td>
<td>2876</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (CH$<em>2$)$</em>{sym}$</td>
<td>2864</td>
<td>2857</td>
<td>2855(m)</td>
<td>1473(w)</td>
</tr>
<tr>
<td>$\delta$ (CH$_2$)</td>
<td>1452</td>
<td>1450(sh)</td>
<td>1460</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1445</td>
<td></td>
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<td>1373</td>
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<td>1349</td>
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<td>1304</td>
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<td>982</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>885</td>
<td></td>
</tr>
</tbody>
</table>

229
4.9 Discussion

4.9.1 Cyclopentene

The spectra recorded during cyclopentene adsorption at low temperature were recorded with the crystal temperature at 173K. This is within the temperature range of liquid cyclopentene, and hence the multilayer spectrum may be expected to be similar to that of the liquid cyclopentene. A comparison of the frequencies observed for liquid cyclopentene [161, 220] can be made. Adsorption of cyclopentene on the surface may lower its symmetry further. In the gas phase its vibrational spectrum was interpreted in terms of $C_{2v}$ symmetry (although the slight bending away from planar which exists would reduce the symmetry to $C_s$). A reduction in symmetry from $C_{2v}$ to $C_s$ would lead to the $B_2$ modes under $C_{2v}$ symmetry, forbidden by the metal surface selection rule, to becoming infrared active. The observation of $A_1$ and both $B_1$ and $B_2$ vibrations in the RAIRS spectra suggest that the symmetry of the adsorbed cyclopentene is lower, i.e. $C_1$ symmetry.

Low coverage spectra were obtained prior to the onset of multilayer adsorption. Bands in low coverage spectra are expected to be more influenced by the presence of the metal substrate than those in the multilayer spectra. No attempt was made to calibrate coverage in this study since it is difficult to define the onset of multilayer adsorption. This could be done by observing any discontinuity in band position / relative intensity as a function of exposure. However, it is difficult to observe any such discontinuity without doing a more detailed experiment, recording a detailed series of spectra.

The bands in the submonolayer and multilayer spectra of cyclopentene were assigned as listed in Table 4–6. The assignment was made with reference to the literature frequencies listed in Table 4–3. The RAIRS spectra were recorded at higher resolution than the reported EELS spectra, and hence the assignment can be made more specifically. A difference from
the EELS spectra is that the 'soft' band was not seen in this RAIRS study. Reasonable agreement with the DRIFTS spectra in the $\nu$ (CH) region exists.

Initially, the strongest band, albeit only 0.0005 Absorbance units, was observed at 2841 cm$^{-1}$, and is assigned as the $\alpha$-CH$_2$ symmetric stretching vibration (where $\alpha$ refers to the carbon atoms adjacent to the double bond). The low signal to noise ratio in the first spectrum (Figure 4–22) is due to the spectrum being recorded at very low coverage. The observation of vibrations at 3048 and 3055 cm$^{-1}$ is in contrast with Avery's EELS studies, indicating that the molecule retains its alkene character on adsorption and is not observed to rehybridise to an alkane like species in this RAIRS study. Avery reported bands due to an alkene species at 3085 cm$^{-1}$, of weaker intensity than expected, due to $\nu$ (=CH), 1630 cm$^{-1}$ due to $\nu$ (C=C) and 700 cm$^{-1}$ in the monolayer EELS spectrum of cyclopentene on Pt(111), although a weak band at 3080 cm$^{-1}$ was observed in the multilayer spectrum, indicating at least some contribution from cyclopentene not rehybridised at the alkene carbon atoms. In general, the bands observed in the low coverage spectrum are comparable in peak positions to the multilayer spectra, but the band intensities do vary slightly, suggesting a sub-monolayer spectrum.

As for liquid cyclopentene, the 3057 cm$^{-1}$ band is less intense than the main group of CH stretching vibrations. The EELS spectra reported by Avery are of poorer resolution than the RAIRS spectra, and the EELS bands cannot be resolved to be assigned to specific vibrational modes, as can be done in this RAIRS study. The EELS bands are thus composed of several overlapping bands, and are only generally assigned as a type of vibration [e.g. $\nu$ (CH)] whereas in RAIRS, the $\nu$ (CH) vibration can be resolved into symmetric and asymmetric modes. There was no evidence of the soft $\nu$ (CH) band, discussed earlier, seen for cyclopentane using EELS, at 2695–2750 cm$^{-1}$ [136] and RAIRS [151], in any of the RAIRS spectra recorded, although such soft bands are known to be more difficult to observe using RAIRS than with EELS [151]. Vibrations at lower wavenumber, generally weaker than those in the $\nu$ (CH) region, were initially observed at 1044,
1203, 1294 and 1350 cm\(^{-1}\), corresponding with the strongest bands observed in this region in the literature cyclopentene spectra.

Between the bands above 3000 cm\(^{-1}\) and the adjacent set of peaks, the baseline in the submonolayer spectrum dips below the otherwise flat baseline in that region. This may be due to the Christiansen Effect, resulting from a change in reflectivity in the region of the absorbance band. This is common in reflection spectra where there is a change in the refractive index of the material on going through an absorption band. This effect is also apparent later, when the change in baseline is in the opposite direction.

Increased exposure led to a strengthening of previously observed bands, with some small shifts in frequency in some bands, as listed in Table 4–6. The 2949 cm\(^{-1}\) band came up in intensity relative to 2847 cm\(^{-1}\) band, suggesting it may be due to an asymmetric vibration, and attenuated by the operation of the metal surface selection rule where the influence of the metal is strong, although this will depend on the thickness of the film. A comparison of relative intensities of the bands observed in the RAIRS spectrum, Figure 4–28 with the FTIR spectrum of solid cyclopentene recorded at 96 K [214], and reproduced in Figure 4–18, show similar relative intensities, although a detailed description or assignment was not given in that study.

On heating to 273K, the strongest remaining bands were CH stretching vibrations, as shown in Figure 4–31 with the 2928 cm\(^{-1}\) band brought up in relative intensity. Further heating, as described in Section 4.9.1 showed no evidence of cyclopentadienyl formation, but the observation of weak \(\nu\) (CH) vibrations as described. The bands above 3000 cm\(^{-1}\) are not observable above 423K suggesting that any alkene remaining on the surface has desorbed or broken up. There is no evidence of cyclopentadienyl formation in this RAIRS study. This is in contrast with Avery's EELS data, where cyclopentadienyl formation was observed on Pt(111) after heating the crystal and adsorbed cyclopentene to 370K. The characteristic vibrational bands of cyclopentadienyl were listed in Table 4–4. In this RAIRS study, heating the crystal results in desorption of most of the adsorbed cyclopentene, with only weak
Figure 4.18: FTIR Spectrum of cyclopentene recorded at 96K, from [214].
vibrational bands remaining. These weak bands were further investigated by recording a series of blank spectra at increasing temperatures. The shift in the baseline of the high temperature spectra suggests that the bands are indeed real, and probably due to hydrocarbon fragments on the surface, although some element of miscancellation does exist between spectra recorded at greatly differing temperatures.

The observation of these small peaks in some spectra must be borne in mind when analysing spectra of low quantities of adsorbates on the single crystal surface. These bands may arise from miscancellation between two spectra recorded at different temperatures, particularly when one spectrum is recorded at elevated temperature and ratioed against a background spectrum recorded at low temperature. Some small absorption features are apparent just below 3000 cm\(^{-1}\) in the RAIRS single beam spectrum shown in Figure 4–17. This is due to residual hydrocarbon on the mirrors, lens and windows in the path of the infrared beam.

In the spectra recorded at ambient temperature (303K), the very weak peaks observed were, if anything, consistent with molecularly adsorbed cyclopentene with no evidence of cyclopentadienyl formation. Under \(1 \times 10^{-8}\) mbar flowing cyclopentene, extremely weak bands were observed in the CH stretching region, at 3063, 2956, 2925, 2900, 2848 and 2820 cm\(^{-1}\), and a very weak peak at 1046 cm\(^{-1}\). From this study it was concluded that cyclopentene did not readily adsorb on Pt(111) as an infrared observable species at 303K. It may have dehydrogenated/dissociated to form carbonaceous deposits on the surface, not detectable using RAIRS as any Pt–C vibrations would be well below the detector cut-off, or may not adsorb in sufficient quantity to be detectable using RAIRS.

The RAIRS spectra of cyclopentene adsorbed on Pt(111) can be compared with the DRIFTS spectra of cyclopentene on EuroPt-1 described in Chapter 3. The position of the bands seen in DRIFTS is included in Table 4–6. One of the DRIFTS spectra from the series of cyclopentene adsorbed on EuroPt-1 is shown together with a RAIRS spectrum in Figure 4–19 for com-
Figure 4–19: (a) DRIFTS spectrum of cyclopentene on EuroPt-1 and (b) RAIRS spectrum of cyclopentene on Pt(111).

This shows the generally broad peaks seen in the DRIFTS spectra on the supported, due to the overlapping contributions to the peaks and surface inhomogeneity, as discussed in Chapter 3. There is no complication from support material in the RAIRS spectra, and this can be used to assist in the assignment of bands on the metal component of the supported catalyst. The band at 2801cm$^{-1}$ seen in DRIFTS is not seen in RAIRS, suggesting that its observation may be connected with the presence of the support. The 2850cm$^{-1}$ band seen in DRIFTS is much narrower than the other DRIFTS peaks, and is of similar linewidth to the 2847cm$^{-1}$ band in the
RAIRS spectrum. The RAIRS spectrum gives an insight into peaks which may be encompassed under the DRIFTS peaks.

In summary, the RAIRS study has shown that cyclopentene readily adsorbs on Pt(111) at low temperature (~173K) as a molecular species. No evidence for rehybridisation at the alkene carbon atoms was observed. Exposure to increasing pressures of cyclopentene resulted in the buildup of a multilayer, giving rise to stronger absorption bands with increasing exposure. Subsequent heating resulted in the evaporation of the multilayer, but no formation of C₅H₅ by dehydrogenation on the surface was observed. The 3053cm⁻¹ peak lost all intensity by 423K, in contrast with the DRIFTS study described in Chapter 3 where the 3063cm⁻¹ band persisted until ~573K.

4.9.2 Cyclopentane

The interaction of alkanes with a metal substrate is relatively weak, as observed previously [208]. The strongest bands observed for the free molecule are also the most intense bands seen following adsorption. Cyclopentane would be expected to adsorb molecularly on Pt(111) as seen in previous studies. The RAIRS spectra recorded in this study support this. Solid cyclopentane exists in three crystal forms in different temperature regions [167]. Type I exists from 181K → 143K, type II, a disordered plastic phase, exists between 138K → 121K and type III, an ordered phase, below 121K. The RAIRS spectra described in this study were all recorded with the crystal temperature between 135 and 128K, in the temperature range for type II solid cyclopentane to exist.

Exposure of the crystal, at 135K, to increasing pressures of cyclopentane resulted in the observation of strong bands in the υ(CH) region at 2954, 2921 and 2864cm⁻¹. On increasing the surface coverage to multilayer coverage, a total of three bands eventually emerge in the deformation region. These bands were observed at 1452, 1315 and 897cm⁻¹ in the multilayer spectra. In general, the frequencies of the observed bands vary slightly from those
reported in previously reported EELS spectra and Chesters’ RAIRS spectrum. The vibrations can be assigned with reference to Avery’s EELS study on Pt(111) and with the literature vibrational frequencies of cyclopentane.

The RAIRS spectra can also be compared with the DRIFTS spectra of cyclopentane on EuroPt-1 described in Chapter 3, where vibrations at 2949 and 2859 cm\(^{-1}\) were assigned as \(\nu\) (CH\(_2\)) asymmetric and \(\nu\) (CH\(_2\)) symmetric vibrations respectively. This suggests that the 2952 and 2864 cm\(^{-1}\) bands seen for multilayer cyclopentane on Pt(111) in the RAIRS study are due to the asymmetric and symmetric \(\nu\) (CH\(_2\)) vibrations. The frequencies of bands observed in the DRIFTS study are included in Table 4–7. There is good agreement between the band positions observed using RAIRS and DRIFTS.

A spectrum from the DRIFTS series recorded during adsorption of cyclopentane on EuroPt-1 is shown in Figure 4–20 with a multilayer RAIRS spectrum of cyclopentane on Pt(111). The 2949 cm\(^{-1}\) band is not present in the particular DRIFTS spectrum shown, but was transiently observed following a pulse of cyclopentane. Comparison with the RAIRS spectrum shows a strong band at 2952 cm\(^{-1}\), assigned as a \(\nu\) (CH\(_2\)) vibration as described above. As with cyclopentene, the band seen in DRIFTS at 2804 cm\(^{-1}\) was not observed in the RAIRS spectrum.

The shift in the baseline in the \(\nu\) (CH) region seen in the low temperature cyclopentene RAIRS spectra was again apparent, although not as marked in this instance. The series of sharp negative absorption peaks seen in the spectra between 1350 and 2100 cm\(^{-1}\) is due to miscancellation between recording the background spectrum and the cyclopentane spectrum. This was due to fluctuating gas phase water levels in the evacuated environment within the spectrometer. Another spectrum was recorded after adsorption, desorption and cooling the sample to the original temperature, but the use of this spectrum as the background spectrum did not eliminate the water absorption bands.

Exposure to higher pressures of cyclopentane resulted in strengthening of the bands described above, seen at low exposure, without significant
Figure 4–20: (a) DRIFTS spectrum of cyclopentane adsorbed on EuroPt-1 and (b) RAIRS spectrum of cyclopentane on Pt(111).
changes in relative intensities or band positions. Heating the crystal to 303K following adsorption resulted in loss of intensity of all bands, indicating straightforward desorption of cyclopentane by this temperature. No dehydrogenation of surface species was observed, as was seen by Avery for cyclopentane on Pt(111) using EELS, where adsorbed cyclopentane partially desorbed and partially dehydrogenated to cyclopentene [139].

There was also no evidence in the RAIRS spectra of the soft $\nu$ (CH) band seen by Avery using EELS [139] and by Chesters using RAIRS [151] for cyclopentane on Pt(111), or by Hoffmann for cyclopentane on Ru(001) studied using EELS [153].

In conclusion, cyclopentane was observed to readily adsorb molecularly on Pt(111) at $\sim$133K. As with cyclopentene, exposure to increasing pressures resulted in the build up of many layers on the surface. No evidence was observed for any soft CH band. Following adsorption, heating the crystal resulted in molecular desorption by 303K, without dehydrogenation to cyclopentene or to the cyclopentadienyl species.

4.9.3 Methylcyclopentane

The spectra observed for methylcyclopentane can be compared with those for cyclopentane. The envelope of peaks in the $\nu$ (CH) region shows six distinct peaks with one shoulder, compared with the two peaks and a shoulder for cyclopentane. The presence of the methyl group lowers the symmetry from $D_{5h}$ for cyclopentane to $C_3$ for methylcyclopentane. This results in three types of inequivalent carbon atoms in the methylcyclopentane molecule, and five inequivalent C-H bonds. Consequently, a more detailed infrared spectrum is observed, compared with the relatively simple spectrum from the more highly symmetrical cyclopentane molecule.

In the RAIRS spectra of cyclopentane discussed earlier, the $\nu$ (CH) vibrations were always of lower intensity than the $\nu$ (CH$_2$) vibrations. The presence of the methyl group in the molecule would be expected to lead
to some additional bands in the spectrum, as compared with that from cyclopentane. In methylcyclopentane, there are two types of -CH₂- groups, compared with five equivalent -CH₂- groups in methylcyclopentane. Hence, splitting of the -CH₂- bands observed for cyclopentane is expected in the methylcyclopentane spectra. Additional bands are also anticipated for the C-H vibrations within the methyl group. Additional bands are indeed observed in the methylcyclopentane spectrum, at 2945, 2920 and 2867 cm⁻¹.

A comparison of the RAIRS spectra recorded of methylcyclopentane on Pt(111) can be made with the DRIFTS spectra reported in the previous chapter. An example of each is shown in Figure 4–21. Both cyclopentane and methylcyclopentane on silica showed similar absorption bands. However, on EuroPt-1 the DRIFTS spectra for the two molecules were quite different. The 2855 cm⁻¹ band observed for methylcyclopentane on EuroPt-1 was assigned as the ν(CH₂) symmetric vibration, enhanced in intensity in the presence of the metal. The 2907 cm⁻¹ band was assigned as the symmetric ν(CH₃) vibration, also brought up in intensity on the metal surface. Hence the bands observed for methylcyclopentane were assigned as listed in Table 4–8. The 2957 and 2945 cm⁻¹ bands are probably ν(CH₂) asymmetric vibrations from the two types of -CH₂- groups, with the bands at 2876 and 2857 cm⁻¹ the corresponding CH₂ symmetric vibrations. The ν(CH₃) vibration may be at 2934 cm⁻¹. The major differences between the region below 1700 cm⁻¹ in the cyclopentane and methylcyclopentane RAIRS spectra are that there were only three bands seen for cyclopentane while many more are seen for methylcyclopentane. The strongest of these are at 1460, 1445 and 1373 cm⁻¹. For cyclopentane, the 1452 cm⁻¹ band was assigned as a CH₂ deformation, and deformation modes for methylcyclopentane must be similar. However it is difficult to assign all individual modes without a detailed gas phase or liquid spectrum of methylcyclopentane. As for both cyclopentene and cyclopentane, the band assigned as an overtone or combination band, seen at 2808 cm⁻¹ in DRIFTS was not observed in the RAIRS study. Heating the crystal following adsorption resulted in molecular desorption with no
Figure 4-21: (a) DRIFTS spectrum of methylcyclopentane adsorbed on EuroPt-1 and (b) RAIRS spectrum of methylcyclopentane on Pt(111).
dehydrogenation or other surface chemistry observed, leaving no infrared detectable surface vibrations.
Figure 4-22: R.A.I.R.S. spectrum of Pt(111) under $1 \times 10^{-9}$ bar cyclohexene at 173K (3150 – 2750 cm$^{-1}$).
At 173K (3150 \rightarrow 2750 \text{cm}^{-1}),

Figure 4-23: RAIRS spectrum of P(111) under 5 \times 10^{-9} mbar cyclopentene

<table>
<thead>
<tr>
<th>Wavenumbers (cm(^{-1}))</th>
<th>Absorbance</th>
</tr>
</thead>
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<tr>
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<td></td>
</tr>
<tr>
<td>2800</td>
<td></td>
</tr>
<tr>
<td>2750</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-24: RAIRS spectrum of Pt(111) under 5×10⁻³ mbar cyclopentane at 173K (1650 - 850 cm⁻¹).
Figure 4-25: RAIRS spectrum of PI(111) under 5 x 10^-9 mbar cyclohexene at 1173K (3150 - 2950 cm^-1).

Absorbance

Wavenumbers/cm^-1

3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
At 173K (3150 – 2750 cm\(^{-1}\)).

Figure 4-26: RARS spectrum of P(111) under 1 \(\times\) 10\(^{-8}\) mbar cyclopentene.
Figure 4.27: RAIRS spectrum of Pt(111) under 1×10⁻⁸ mbar cyclopentene at 173K (1650 - 850 cm⁻¹).
Figure 4.28: RAIRS spectrum of Pt(111) under 1×10⁻² mbar cyclopentene at 173K (3150 ~ 950 cm⁻¹).
Figure 4-29: RAIRS Spectrum of cyclopentene on Pt(111) at 223K (3150 – 2750 cm⁻¹)
Figure 4: RAIRS spectrum of cyclopentene on Pt(111) at 223K

(1650 - 850 cm\(^{-1}\))
Figure 4-31: RAIRS Spectrum of cyclopentene on Pt(111) at 273K (3150 – 2750 cm⁻¹).
Figure 4-32: RAIRS Spectrum of cyclopentene on Pt(111) at 293K (3150 → 2750 cm⁻¹).

Wavenumbers/cm⁻¹

Absorbance
Figure 4-33: RAIRS Spectrum of cyclopentene on Pt(111) at 423K (3150 – 2750 cm\(^{-1}\)).
Figure 4-34: RAIRS Spectrum of cyclopentene on Pt(111) at 623K (3150 - 2750 cm⁻¹).
Figure 4-35: RAIRS Spectrum of clean Pt(111) at 273K (3150 – 2750 cm⁻¹).
Figure 4-36: RAIRS Spectrum of clean Pt(111) at 323K (3150 – 2750 cm\(^{-1}\)).
Figure 4.37: RAIRS Spectrum of Clean P4(111) at 423K (3150 - 2750 cm⁻¹).
Figure 4-38: RAIRS Spectrum of clean Pt(111) at 623K (3150 → 2750 cm$^{-1}$).
Figure 4-39: Raman spectra during exposure of Pt(111) to (a) 5 x 10^{-9} mbar, (b) 1 x 10^{-8} mbar, and (c) 1 x 10^{-9} mbar showing cyclopentene at 2930 cm^{-1}.
Figure 4.40: RAIRS spectrum of Pt(111) under $5 \times 10^{-10}$ mbar cyclopentane at 135K (3050 - 2750 cm$^{-1}$).
Figure 4.41: RAIR spectrum of Pt(111) under 9 \times 10^{-10} mbar cyclopentane at 133K (3050 – 2750 cm^{-1}).
at 131K (3060 → 2760cm$^{-1}$)

Figure 4-42: RAIRS Spectrum of Pt(111) under 2x10−9 mbar cyclopentane

Absorbance

Wavenumbers/cm$^{-1}$

3050
3000
2950
2900
2850
2800
2750
Figure 4.43: RALRS spectrum of Pt(III) under 1 x 10^-8 mbar cyclopendane at 128K (3050 - 2750 cm^-1).
Figure 4.44: RAIRS spectrum of Pt(111) under $1 \times 10^{-3}$ mbar cyclopentane at 128K (1650 - 850 cm$^{-1}$).
at 128K (3060 ~ 900 cm⁻¹).

Figure 4-45: RARS spectrum of Pt(111) under 1 x 10⁻⁸ mbar cyclopentane
Figure 4.46: RAIRS spectrum of Pt(111) under 5x10^{-10} mbar methylyclopentane at 118K (3050 – 2750 cm^{-1}).
Figure 4.47: RAIRS spectrum of Pt(111) under $1 \times 10^{-3}$ mbar methyldipentane at 117K (3050 → 2750 cm$^{-1}$).
Cisopentane at 1172K (9050 \to 2760 \text{ cm}^{-1}).

Figure 4.6: RAIRS spectrum of Pt(111) under 1 \times 10^{-8} mbar methylene.
Figure 4-49: RAIRS spectrum of Pt(111) under 1×10⁻⁸ mbar methylyclopentane at 117K (1650 - 1250 cm⁻¹).
copernicite at 117K (3.050 \to 1150 \text{cm}^{-1}).

Figure 4-50: RALRS spectrum of Pt(III) under 1 \times 10^{-8} \text{mbar metal}

- Wavenumbers/cm\(^{-1}\)
- Absorbance

Absorbance: 0.005
Figure 4.51: RAIRS spectrum of Pt(111) under 5×10⁻⁸ mbar methylyloctane at 113K (3050 – 2750 cm⁻¹).
Figure 4-52: R.AIR spectrogram of P(111) under 5 x 10^-9 mbar methlyc FCD.

To: Figure 113K (1650 - 850 cm^-1),

Wavenumbers/cm^-1:

- 1600
- 1500
- 1400
- 1300
- 1200
- 1100
- 1000

Absorbance

0.005
Figure 4-53: RAIRS spectrum of Pt(111) under \(5 \times 10^{-8}\) mbar methylcyclopentane at 113K (3050 – 850 cm\(^{-1}\)).
Chapter 5

Conclusions

The exchange experiments of methylcyclopentane with deuterium described in Chapter 2 essentially use post reaction analysis to determine how the methylcyclopentane molecule adsorbs and reacts on the catalyst. As such, deuterium is used as a ‘label’ and information on its concentration and location in an exchanged hydrocarbon molecule reveals intermediates and favoured reaction paths. The exchange experiments were carried out under controlled high vacuum conditions, and were designed to react at a rate by using a small amount of catalyst of low surface area, where the reaction could be followed using mass spectrometry, and allowed to run to a suitable extent to optimise analysis of the products using 2D NMR Spectroscopy.

An important consideration in the three different experiments described in this Thesis is that of the experimental timescale. This ranges from the very short lived surface species involved in the exchange experiments to the long time involved in the collection of a RAIRS spectrum. Typical lifetimes of the intermediates in the exchange studies are of the order of $10^{-4}$ seconds, assuming that reaction and desorption are rapid with respect to adsorption. The gas phase products are monitored in this type of experiment, and thus no information is available on any species which may remain adsorbed on the surface.

The catalysts used for the exchange experiments are all 1% metal loading, and have too low a metal loading and metal surface area for adsorption on the
metal to be observed using DRIFTS or transmission infrared spectroscopy. Some experiments using DRIFTS to study adsorption on the catalysts used for the NMR experiments revealed only adsorption on the silica support of these catalysts, and no vibrations due to adsorption on the metal were observed.

In the exchange experiments, CH bond scission occurred allowing incorporation of a number of deuterium atoms into the hydrocarbon molecules. Information on the number and distribution of these deuterium atoms was then used to deduce the predominant reaction mechanisms and most favourable adsorbed intermediate species involved in the exchange of hydrogen atoms for deuterium atoms.

In the DRIFTS and transmission experiments, infrared spectroscopy is used *in situ* as a probe to observe (infrared observable) vibrations due to adsorbed species on both the metal and on the support. A high surface area catalyst is necessary to achieve sufficient sensitivity in this type of experiment, in contrast with the catalysts used in the exchange experiments, designed primarily to react at a controlled rate. The experiments described in this study showed molecular adsorption on cyclopentene, cyclopentane and methylcyclopentane on silica alone, and on both the silica support and the metal component of EuroPt-1 (a Pt/SiO₂ catalyst). EuroPt-1 proved suitable for infrared experiments with a relatively high metal loading of 6.3% and a dispersion of 60%. Although the silica support blacked out any CH deformations, this could be overcome using an alumina supported catalyst, which blacks out infrared below ~1150cm⁻¹ in DRIFTS and 1100cm⁻¹ in transmission. However, much information was gained from the study of adsorption on the Pt/SiO₂ catalyst. In DRIFTS, enhancement of specific absorption bands on EuroPt-1, *i.e.* on the metal, indicated the operation of the metal surface selection rule for all three molecules in this study. The estimated heats of desorption showed the molecules to be more strongly held on the metal than on the silica support. Although the observation of species with infrared spectroscopy does not imply that they are catalytically active,
together with parallel information on formation of gas phase products, the identity of the species observed on the surface can often be deduced. Thermal conductivity and mass spectral observation of the gas phase molecules was used to support the infrared spectra in this study.

Cyclopentene adsorption on EuroPt-1 was studied using both DRIFTS and transmission infrared spectroscopy, and the relative intensities of the CH stretching vibrations showed a striking difference. The symmetric CH$_2$ vibration at 2850 cm$^{-1}$ from cyclopentene adsorbed on platinum was enhanced with respect to the asymmetric CH$_2$ vibration at 2955 cm$^{-1}$ in the DRIFTS study, but the intensities of the corresponding bands in transmission were reversed. This is probably as a result of the different diffusion behaviour of the adsorbate in both samples. Diffusion will be much more rapid in the loosely packed catalyst bed in the DRIFTS cell than in the compressed transmission disc. Weakly held species will be swept away more rapidly in the DRIFTS experiment than in the transmission cell, and gas phase or liquid species held within the pores of the transmission disc may account for the different peak intensities in the transmission spectra. A more detailed study on diffusion could be carried out to investigate the difference between DRIFTS and transmission. Further study could also be made of cyclopentene adsorption on a silica disc using transmission infrared spectroscopy, and by doing corresponding studies with other molecules.

Exchange type experiments could be designed for infrared study. Hydrocarbon and deuterium could be mixed in the gas handling line and injected into the flow system. A high metal loading catalyst would be needed in order for adsorbates to be infrared detectable, and this would make reaction rates high. However, intermediates would probably be too short lived to be detectable on the timescale of a typical DRIFTS experiment. The gas flow system could be redesigned to be a recirculating system to be used for exchange type experiments. Deuterium labelled hydrocarbon molecules could be used to further investigate CH vibrations.

In the DRIFTS and transmission infrared experiments, the adsorbed
species are observed in situ and the gas phase can be monitored simultaneously to support the infrared observations. A spectrum typically took 25 seconds to record, so there is no chance of observing any short lived adsorbed species, such as those probed in the exchange experiments, in this type of study. A DRIFTS spectrum will be time averaged, showing the average population on the catalyst during the time taken to record the spectrum. This may be a static population resident on the surface throughout the data collection or it may be the average of a dynamic population present for some time during data collection. The decay of band intensities observed in the DRIFTS spectra suggests that at least some species are swept out of the cell as the series of spectra is collected. The persistence of observed species could be investigated over a longer timescale. The DRIFTS spectra were recorded at ambient temperature and above, but recording spectra at lower temperatures may lengthen the surface lifetime of any static species, and may correlate better with the exchange experiments. A high dynamic population would only be observable in DRIFTS under continual high pressure exposure to the adsorbate.

Following previous single crystal work, formation of the cyclopentadienyl species, C_5H_5, upon heating adsorbed cyclopentene on platinum was anticipated. Evidence from the DRIFTS study of cyclopentene on EuroPt-1 suggests that the cyclopentadienyl species was formed following heating to \( \sim 573 \) K, indicated by the persistence of the band at 3063 cm\(^{-1}\) when all other bands had decayed to zero intensity. During heating, the symmetric CH\(_2\) vibration due to cyclopentene on platinum lost intensity with concomitant formation of two small bands at 2932 and 2909 cm\(^{-1}\). The identity of these bands has not yet been positively established, although hydrogenation experiments suggest them to be due to unsaturated species.

Cyclopentane showed no evidence of dehydrogenation to cyclopentene or to the cyclopentadienyl species in DRIFTS, as was previously observed on Pt(111) using EELS. Facile molecular desorption of both cyclopentane and methylcyclopentane was observed from EuroPt-1.
The RAIRS spectra discussed in Chapter 4 were recorded for adsorption on a Pt(111) single crystal during exposure in ultra high vacuum conditions, somewhat different from the flow conditions used in the DRIFTS and transmission study on the supported metal catalysts. The Pt(111) surface is well defined and clean on the atomic level, in contrast with the inhomogeneity of the metal surfaces of a supported metal catalyst.

Typically, pressures of up to $10^{-8}$ mbar of adsorbate were used in the RAIRS experiments compared with pulses of $10^{-10}$ atm in the supported catalyst experiments. Another difference is that the single crystal experiments generally have to be carried out at low temperature in order to reach sufficient coverage on the single crystal to be detectable using RAIRS, in contrast to the DRIFTS experiments carried out at $\sim 300$K. Hence, it is not surprising that some differences may be expected between UHV studies on well defined single crystal surfaces and with the poorly defined supported metals, which also has features due to the presence of the support.

The RAIRS experiments with the same three hydrocarbon molecules showed them to be readily adsorbed, molecularly, at low temperature. RAIRS showed no evidence of dehydrogenation of cyclopentene to C$_5$H$_5$ on heating. Instead, molecular desorption occurred. Weak absorption bands were observed at low coverage, and exposure to higher quantities of cyclopentene allowed the build-up of many layers on Pt(111) as observed using RAIRS.

The reasons for observation of the cyclopentadienyl species using EELS, and in the DRIFTS study but not using RAIRS must be further investigated. A fundamental difference between the EELS experiment and the RAIRS experiment is that EELS spectra are not usually recorded with the crystal held at high temperature. Instead, the crystal is flashed to the desired temperature and then cooled to record the spectrum. This allows for the possibility of readsoption of desorbed/other species since the increase in pressure from desorption is not immediately pumped away. This could lead to observation of 'trapped' species that would have desorbed and been pumped away in the RAIRS experiment. As mentioned in Chapter 4, this can be overcome by
heating the crystal by other means. In RAIRS, the crystal is usually heated to the desired temperature and held at that temperature while the spectrum is recorded, but the comparable experiment to the EELS procedure could be done easily. Further investigation of this could also be made utilising the facility of the high pressure cell, recording RAIRS spectra under pressures up to several atmospheres to investigate the adsorbed species supported under these conditions. Hydrogenation or deuteration of unsaturated surface species could also be investigated using mass spectrometry. The more reactive chemistry seen by Avery following adsorption of cyclopentene on his Pt(111) single crystal, and also in the study of cyclopentane adsorption may be in part due to the state of the 'clean' crystal surface, e.g. differing proportions of defect sites between that crystal and the one used in this study.

Cyclopentane and methylcyclopentane also showed molecular adsorption and a build-up of many layers on the surface. Heating then resulted in molecular desorption. No observation of the strong soft CH vibration was seen in any of the RAIRS spectra reported. This is particularly perplexing since it has been reported previously for cyclopentene on Pt(111) studied with EELS, and for cyclopentane on Pt(111) observed using EELS and RAIRS, and on Ru(001) using EELS. The soft band is more difficult to detect using RAIRS than EELS, but has been seen using RAIRS, and the reasons for it not being observed in this study merit further attention and investigation.

Since EuroPt-1 metal particles are made up of a range of metal faces, a comparison of a RAIRS investigation of cyclopentene (and other molecules) on other single crystal surfaces e.g. (100), (110), stepped surfaces may reveal some further information and changes in band frequencies. A detailed TPD study, multiplexing m/z = 2 (H₂) and 67 (cyclopentene) in parallel with RAIRS may reveal differences between the chemistry observed in this study with that previously observed by Avery and Henn. Study could also be extended to other metals to investigate any variation in chemistry with the metal surface.
In the RAIRS experiment, the typical experimental timescale is very much longer than the two regimes described above. It is of the order of tens of minutes, although the spectral acquisition time could be shortened by compromising on the signal to noise ratio by reducing the number of scans recorded. Pressures used are typically very low, and can be calibrated doses or continual flow. In this case, only long lived static species can be observed. *In situ* high pressure RAIRS experiments could be used to reveal the time averaged dynamic population.
References


287


[134] Digilab Division Bio-Rad. Cambridge, MA, US.


291


## Appendix A

### Purity and suppliers of gases and chemicals

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<th>Purity</th>
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Appendix B

Properties of EuroPt-1

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<td>EuroPt-1 is a 6.3% Pt/SiO₂ catalyst prepared by ion exchange by Johnson Matthey plc.</td>
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<tr>
<td>Total (BET) surface area = 185 +/- 5 m²g⁻¹</td>
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<td>Surface area of silica support = 364 +/- 5 m²g⁻¹</td>
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<td>Size distribution of platinum particles, 1.0 → 3.5nm, centered at 1.8nm</td>
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<td>75% of particles ≤ 2.0nm diameter</td>
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<td>Dispersion = 60%</td>
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Appendix C

Published Work
Reactions of Methylcyclopentane over Supported-metal Catalysts

Ronald Brown, Anne S. Dolan, Charles Kemball* and Gordon S. McDougall*
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

The exchange reaction of methylcyclopentane with deuterium has been carried out over supported palladium, platinum and rhodium catalysts and the products analysed by mass spectrometry and deuterium NMR spectroscopy. The NMR resonances for the deuterium in the six positions in the molecule were well separated and each could be resolved into two or more components as a consequence of the isotopic shifts due to the presence of neighbouring deuterium atoms.

It was possible to determine the fractions of the molecules exchanged on the open side of the ring, on the hindered side (cis to the methyl group) or on both sides. These fractions and other features of the experimental results were used to discuss the mechanisms of the exchange reactions and the manner in which these varied with the metal or with temperature. The highest extents of multiple exchange and of 'turnover' of the molecules on the surface were found with palladium.

The essential features associated with the exchange of methylcyclopentane with deuterium over palladium catalysts were discovered many years ago by Burwell et al. and helped to establish the nature of one of the main mechanisms which gives rise to multiple exchange on palladium and on other metals as well. This mechanism, sometimes called the αβ-process, involves interconversion on the catalyst surface of adsorbed alkyl radicals and adsorbed alkene molecules. It is relatively more efficient on palladium than on other metals; maxima in the distributions of isotopic products are found corresponding to the completion of the exchange of sets of all hydrogen atoms which can be replaced by the αβ-process. Thus for methylcyclopentane, there is a maximum at the D₄ product corresponding to exchange of the four hydrogen atoms cis to the methyl group, i.e. on the hindered side of the molecule. There is also a maximum in the D₄ product corresponding to the exchange of the five hydrogen atoms on the open side of the molecule, i.e. trans to the methyl group, and the three on the methyl group. A further maximum at the D₁₂ product arises from molecules which have exchanged both sets of hydrogen atoms. Propagation of the multiple exchange from one set to the other requires a mechanism other than the αβ-process; this is generally believed to involve the 'turnover' of an adsorbed alkene on the surface and the relative contribution of this process increases with increase of temperature.

The purpose of the present investigation was to examine the exchange of methylcyclopentane with deuterium over a number of supported-metal catalysts using high-field NMR spectroscopy as well as the traditional mass spectrometric technique to analyse the products. Recently, the use of NMR spectroscopy has provided a means of identifying and estimating groupings of deuterium atoms in the products from exchange reactions and such detailed information has proved valuable in defining possible reaction mechanisms. Preliminary investigations showed that methylcyclopentane was an interesting molecule to examine in this way because the chemical shifts of the deuterium atoms in the six positions in the molecule were different, see Fig. 1, and furthermore the spectra for each position could be resolved into a number of resonances resulting from the isotopic shifts caused by varying amounts of neighbouring deuterium atoms. There was a good prospect that the detailed knowledge to be gained by combining NMR and mass spectrometric data would provide more evidence about what is happening in the exchange reactions and how the pattern of behaviour varies with different metals.

Experimental

Most of the experiments were carried out with palladium, platinum or rhodium catalysts, containing 10⁻⁴ mol g⁻¹ of metal on silica, identical to those described recently. Some preliminary experiments were run using a catalyst containing 2.6 x 10⁻⁵ mol g⁻¹ platinum on γ-alumina. Deuterium (99.5%) was supplied by Matheson Gas Products and purified by diffusion through a heated palladium–silver alloy thimble. Methylcyclopentane (Fluka > 99.5%) obtained from Fluorochem Ltd. was degassed before use.

Early experiments were carried out using a static system, but a recirculation system which gave more efficient collection of products for NMR analysis was used subsequently. Each system was connected by a capillary leak to a Vacuum Generators Micromass 601 mass spectrometer. The static system had a volume of 240 cm³ and was used with a hydrocarbon pressure of 3.6 kPa, giving a charge of 2.25 x 10²⁰ molecules, and a deuterium to hydrocarbon ratio of 5:1. The recirculation apparatus had a volume of 360 cm³ and was used with a hydrocarbon pressure of 2.9 kPa, corresponding to a charge of 2.5 x 10²⁰ molecules, and the same ratio of deuterium to hydrocarbon.

The course of each reaction was followed in the mass spectrometer using 25 eV electrons to bring about ionisation. The usual corrections were made for naturally occurring isotopes and for the formation of fragment ions corresponding to the loss of up to five hydrogen atoms from the parent molecule. The total fragmentation over this range amounted to only ca. 7%. Standard methods were used to obtain the initial rates of exchange.

After some 15–20% reaction had occurred, samples of the exchanged hydrocarbons were collected and analysed subsequently by deuterium NMR spectroscopy. Most of these analyses were carried out using a Bruker WH 360 spectrometer operating at 55.28 MHz, but one was also analysed

**Fig. 1** Designations of the six positions for deuterium in methylcyclopentane; chemical shifts, δ (ppm), for these positions are I, 1.84; II, 1.72; III, 1.50; IV, 1.60; V, 1.03 and VI, 0.96
using a Varian VXR 600 S spectrometer operating at 92.13 MHz.

**Results**

Table 1 records the details of the main experiments, including the weight of catalyst, temperature, initial rate of exchange and the composition of isotopic methylcyclopentanes at the stage when the reaction was stopped and the sample taken for NMR analysis.

Steady rates of exchange were found in all cases except with Rh/silica at 333 K for which the usual plot showed curvature and a decrease of rate with time. A complete range of deuterio-products, from the D₁ up to the D₁₂ compound, was observed in each experiment apart from Rh₁ carried out at 291 K. The average deuterium content of the product, $M_\text{r}$, increased with temperature and was higher with palladium than with other metals.

The main features of the NMR spectra are shown in Fig. 2 which gives the results for experiment Pt₁ analysed on both NMR spectrometers. The quantitative data from these spectra are given in Table 2, which summarises the percentages of the total deuterium in the six positions in the molecule and in the different groupings associated with each position. Approximate values of the isotopic shifts which give rise to various resonances associated with deuterium in each position are known from previous work with cyclopentane and with other hydrocarbons. z (two-bond) isotopic shifts, resulting from a second deuterium atom on the same carbon atom, are in the range from -17 to -20 ppb; β (three-bond) shifts, due to deuterium on a neighbouring carbon atom, are from ca. -7 to -9 ppb; γ (four-bond) shifts are only -1 to -3 ppb and can be neglected in most cases. The resonances associated with each position will be described in sequence.

**Position I.** Deuterium in this tertiary position cannot be subject to an α shift but may experience up to seven β shifts; two each from deuterium in positions II and V, and three from deuterium in position VI. The resolution was not complete but both spectra showed evidence for a larger component and a smaller more highly shifted component. The latter probably corresponds to molecules which have exchanged in the methyl group, position VI.

**Position II.** Deuterium in this position may experience one α shift if position V is exchanged and up to three β shifts from deuterium in positions I, III and IV. Three resonances were detected with both spectrometers and can be assigned with confidence. The first, corresponding to between 4 and 5% of the total deuterium, represents molecules exchanged only in position II. The large resonance, ca. 16% of the total deuterium with a shift of -19 ppb, corresponds to molecules multiply exchanged on the open side of the ring. The third resonance with the large isotopic shift between -43 and -50 ppb arises from molecules exchanged on both sides of the ring. Completely exchanged molecules would be expected to show an isotopic shift of $-18 + (3 \times 8) = -42$ ppb or possibly slightly more if γ shifts are included.

**Position III.** The possibilities for deuterium in position III are one α and up to four β shifts. The relative sizes of the three resonances determined with the 360 spectrometer are about the same as for those for position II. A little further resolution was achieved with the 600 spectrometer which enabled the large peak to be separated into two components, ca. 5% with a single β shift and ca. 14% with two β shifts.

**Position IV.** The results are broadly similar to those described for position III although the relative intensities of the resonances are different. Once again further resolution of the main peak into two components was possible with the 600 spectrometer.

**Position V.** Deuterium in this position may experience one α shift but only three β shifts and consequently the isotopic shifts in Table 2 are lower than those for positions III and IV. More complete resolution was obtained with the 600 spectrometer and the three peaks represent (a) molecules exchanged solely in position V, (b) molecules multiply exchanged on the hindered side of the ring with one β shift and (c) molecules exchanged on both sides of the ring. The maximum shift expected for fully exchanged molecules would

![Diagram](image)

**Fig. 2.** Deuterium NMR spectra for methylcyclopentane exchanged on Pt/alumina at 299 K, (a) using the 360 MHz spectrometer, (b) using the 600 MHz spectrometer.

**Table 1** Mass spectrometric analyses of the exchanged methylcyclopentanes subsequently analysed by NMR spectroscopy.

<table>
<thead>
<tr>
<th>exp.</th>
<th>catalyst mass/mg</th>
<th>T/K</th>
<th>initial rate $r/10^{-3}$ molecule s$^{-1}$ (metal atom)$^{-1}$</th>
<th>$D_0$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_3$</th>
<th>$D_4$</th>
<th>$D_5$</th>
<th>$D_6$</th>
<th>$D_7$</th>
<th>$D_8$</th>
<th>$D_9$</th>
<th>$D_{10}$</th>
<th>$D_{11}$</th>
<th>$D_{12}$</th>
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<td>2.2</td>
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<td>1.6</td>
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<td>0.8</td>
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<tr>
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<td>2.8</td>
<td>1.8</td>
<td>1.7</td>
<td>1.6</td>
<td>1.6</td>
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<td>1.6</td>
<td>3.4</td>
<td>4.2</td>
<td></td>
</tr>
</tbody>
</table>

*a The support was alumina. b Pd₁ and Rh₁ were carried out in the static system. c tr = trace amount. d Some reduction in rate was observed.
Table 2  Detailed analyses of the exchanged methylcyclopentanes from experiment Ptl using both NMR spectrometers

<table>
<thead>
<tr>
<th>position of deuterium</th>
<th>$\delta$ (ppm)</th>
<th>$-\Delta$ (ppb)</th>
<th>%</th>
<th>$-\Delta$ (ppb)</th>
<th>%</th>
</tr>
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</tr>
<tr>
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<td>18</td>
<td>3.0</td>
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<tr>
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<td></td>
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<td></td>
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</tr>
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<td>46</td>
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<td>16</td>
<td>3.7</td>
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<td>38</td>
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<td>46</td>
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<td>V</td>
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<td></td>
<td>39</td>
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<tr>
<td>VI</td>
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<tr>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>54</td>
<td>6.1</td>
<td></td>
<td>6.3</td>
<td></td>
</tr>
</tbody>
</table>

* Isotopic shift.  * Average D content of methyl group, $M_{VI} = 1.7$.  * $M_{VI} = 1.8$.

be $-\lfloor 18 + (3 \times 8) \rfloor = -42$ ppb or possibly slightly more if $\gamma$ shifts are included. The 360 spectrometer did not resolve the first two peaks.

**Position VI.** Deuterium in the methyl group can be subject to only one $\beta$ shift and up to two $\alpha$ shifts. The values for shifts in Table 2 indicate that the $\beta$ shift has a larger value than usual of $-12$ ppb and the $\alpha$ shifts are ca. $-20$ ppb, in line with those found for other non-cyclic saturated hydrocarbons. The four peaks are readily identified and correspond to the groupings CH$_2$DCH<, CH$_2$CD<, CHD$_2$CD< and CD$_2$CD<, which gave the largest resonance.

The conclusion from the detailed analysis of the products from experiment Ptl using both NMR spectrometers was that adequate information was obtained with the 360 instrument. For the methylcyclopentane-D$_2$ system, little actual gain in resolution or sensitivity was achieved with the higher-field instrument. Some representative NMR spectra of the products from the other experiments are given in Fig. 3 and 4. In most cases, it was possible to recognise two resonances for deuterium in positions II–V and three resonances for deuterium in position VI. The relative amounts of deuterium in the groupings responsible for these peaks are given in Table 3. The spectrum in Fig. 4(a) for experiment Pd1 run at 293 K shows a series of narrow partially resolved peaks corresponding to singly exchanged molecules with deuterium in positions I–IV and in this respect was similar to results shown for Ptl in Fig. 2.

**Interpretation**

The percentages in Tables 2 and 3 for the amounts of deuterium in positions I–VI can be used to work out the relative proportions of the various groupings. The conclusion from the detailed analysis of the products from experiment Ptl using both NMR spectrometers was that adequate information was obtained with the 360 instrument. For the methylcyclopentane-D$_2$ system, little actual gain in resolution or sensitivity was achieved with the higher-field instrument. Some representative NMR spectra of the products from the other experiments are given in Fig. 3 and 4. In most cases, it was possible to recognise two resonances for deuterium in positions II–V and three resonances for deuterium in position VI. The relative amounts of deuterium in the groupings responsible for these peaks are given in Table 3. The spectrum in Fig. 4(a) for experiment Pd1 run at 293 K shows a series of narrow partially resolved peaks corresponding to singly exchanged molecules with deuterium in positions I–IV and in this respect was similar to results shown for Ptl in Fig. 2.

**Fig. 3**  Deuterium NMR spectrum, determined with the 360 MHz instrument, for the products from experiment Rh2

**Fig. 4**  Deuterium NMR spectra, determined with the 360 MHz instrument, for the products from reactions over Pd/silica; (a) Pd1 at 293 K, (b) Pd2 at 333 K
Table 3 Groupings of deuterium atoms in the exchanged methyl-cyclopentanes and average isotopic shifts from analysis using the 360 MHz NMR spectrometer

<table>
<thead>
<tr>
<th>position of deuterium</th>
<th>$-\Delta \delta$ (ppb)</th>
<th>Pt2$^a$</th>
<th>Rh2$^a$</th>
<th>Pd1$^b$</th>
<th>Pd2$^c$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>—</td>
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<td>II</td>
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<td>5.1</td>
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<td>average D content</td>
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<td>2.0</td>
<td>2.2</td>
<td>2.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

of methyl group, $M_{vi}$

* 333 K. $^a$ 293 K. $^b$ These values include the partially resolved peaks corresponding to singly exchanged molecules. $^c$ Measured only for Pt2 but assumed to hold for the other experiments.

The extent of exchange of the different kinds of hydrogen atoms.

To determine the relative exchanges given in Table 4 it is necessary to take into account the fact that position I corresponds to a single atom, position VI to three atoms, and the extent of exchange in this position, shown in Table 4, never exceeded unity and was noticeably lower over platinum and in experiment Rh1. However, the percentages for the component peaks for position VI, given in Tables 2 and 3, can be used to work out the mean number of deuterium atoms in exchanged methyl groups. For example, the value of $M_{vi}$ for Pt1 using the 360 spectrometer is

$$M_{vi} = \frac{3.1 + 1.2 + 2.1 + 6.1}{3.1 + 1.2 + 2.1/2 + 6.1/3} = 1.69$$

The values of $M_{vi}$, so derived, are given in the last line of Tables 2 and 3. They were ca. 1.7 for Pt1 but rose to 2 or more for the experiments analysed in Table 3. These values demonstrate that although the methyl group was not readily exchanged (low relative exchange), those groups which had reacted were extensively exchanged ($M_{vi}$ usually $\geq 2$). This interesting aspect of the results will be discussed below in more detail.

The NMR results in Tables 2 and 3 provide a means of calculating the proportion of the molecules exchanged on the open side, the hindered side or on both sides. The basis of the calculation is that, for most positions, the less shifted resonance corresponds to deuterium in molecules exchanged on only one side and the more highly shifted resonance to deuterium in molecules exchanged on both sides. The calculation will be exemplified for experiment Pt2.

For deuterium in position II the fraction in molecules exchanged on both sides is 8.6/22.3 = 0.39. For deuterium in position III the fraction is 8.9/21.8 = 0.41; and thus the mean fraction of molecules exchanged on the open side and also exchanged on the hindered side is 0.40. Considering the deuterium on the hindered side, position IV has a fraction 11/18.4 = 0.60 exchanged on both sides and the corresponding fraction for deuterium in position V is 7.2/12.2 = 0.59. So an average 0.60 of the molecules exchanged on the hindered side are also exchanged on the open side. If $F_O$, $F_H$ and $F_B$ correspond to the fractions exchanged, respectively, on the open side only, the hindered side only or on both sides, it follows that $F_O + F_H + F_B = 1.00$, $F_B(F_O + F_B) = 0.40$, and hence $F_O = 0.47$, $F_H = 0.21$ and $F_B = 0.32$.

Values of $F_O$, $F_H$ and $F_B$ derived in this way from the results in Tables 2 and 3 are given in Table 5. A further subdivision may be made of the fraction $F_B$ by using the mass spectrometric analyses in Table 1. There will be molecules exchanged on both sides and in the methyl group, i.e. $F_B F_{BM^*$}, and molecules exchanged on both sides but not in the methyl group, i.e. $F_B(1 - F_{BM})$. Since products with from 10 to 12 deuterium atoms must be exchanged on both sides and in the methyl group, the fraction of all the deuteroproducts in the range from $D_{10}$ to $D_{12}$ provides a minimum value for $F_B F_{BM^*}$. This calculation underestimates $F_B F_{BM^*}$ because some molecules, even although exchanged on both sides and in the methyl group, will not have as many as 10 deuterium atoms. Results are included in Table 5.

**Discussion**

The results show some features which are common to all three metals. As shown in Table 4, the usual pattern of rela-
tive exchange is open side > hindered side > methyl group. There is good agreement, Table 5, between the fractions of deuterium in positions II and III in molecules exchanged on both sides, and similar agreement between the corresponding fractions for positions IV and V. In every case, the values for IV and V are greater than those for II and III. An increase of temperature leads to an increase in the average deuterium content of the products (Table 1) and to all the fractions (Table 5) corresponding to molecules exchanged on both sides. Before considering the relevance of the results to the mechanisms of exchange some features relating to the individual metals will be discussed.

**Platinum**

The data in Tables 4 and 5 show that for this metal the pattern of exchange was clearly open side > hindered side > methyl group. It is the metal which showed the most distinctive break in the product distributions (Table 1) after the D₄ compound. This was caused by a significant fraction of the reacting molecules undergoing multiple exchange on the open side of the ring without reaction of the methyl group. Confirmation of this can be obtained by a simple calculation using evidence about the amount of methyl group exchange and this will be exemplified for experiment Pt2. Combining the total percentage of deuterium in position VI of 14.9 and the mass spectrometric result that the average deuterium content of the exchanged molecules was 5.0, it follows that the average deuterium content of the methyl groups in the products was 5.0 x 0.149 = 0.745. However, the last line of Table 3 tells us that the average deuterium content of exchanged methyl groups was 2.0. Hence we can deduce that 63% of the products contained unexchanged methyl groups and the mean deuterium content of these groups was due to the 37% with an average of 2.0 D atoms, since 2.0 x 0.37 = 0.74.

This metal showed clear evidence of a contribution from stepwise exchange in addition to the substantial amounts of multiply exchanged products. Both experiments gave a significant amount of D₃ product (Table 1) and the small NMR resonances in Fig. 2 corresponds to single deuterium atoms in positions II—VI. Platinum frequently gives U-shaped distributions of products and the present results conform to the expected behaviour.

It is unfortunate that the early but detailed Pt1 experiment was carried out on an alumina-supported catalyst. However, the results of Pt1 and Pt2 were broadly similar and show differences which arose mainly from the change of temperature.

**Palladium**

The main characteristics of the results over palladium were the clear breaks after the D₄ compound and the well defined maxima at the D₅ and D₁₂ compounds, in agreement with previous results. The break after D₄ arises from exchange on the hindered side of the ring only. There is little chance of molecules adsorbed on the hindered side on palladium being able to exchange the methyl group because this would involve an αγ-adsorbed intermediate. Results on the exchange of 2,2-dimethylpropane have shown that palladium does not readily form this type of species. In contrast, molecules exchanging by loss of hydrogen from the open side of the ring have a chance of undergoing exchange in the methyl group as well, because the ordinary αβ-process permits this to happen. Palladium is the most efficient of the three metals in catalysing the αβ-process and so shows the greatest tendency to complete the exchange of sets of hydrogen atoms which can be replaced by this mechanism. The maxima at the D₈ compound are a consequence of this characteristic of the palladium catalyst. The results in Table 5 show that palladium is also the most efficient catalyst for bringing about the ‘turnover’ reaction which permits the exchange to occur on both sides of the ring. The last two lines in Table 5 show that the propagation of the exchange to include the methyl group occurs most readily on palladium as well. Calculations based on the deuterium content of the methyl groups show that 34% of all products in experiment Pd1 and 67% of the products in experiment Pd2 were exchanged in the methyl group.

The results in Table 4 indicate that preferential exchange on the open side of the ring, particularly of the tertiary hydrogen in position I, occurred with Pd1 but the reactivity on the hindered side and in the methyl group was similar. In contrast, the results for Pd2 showed evidence of preferential exchange in position IV [see the substantial peak in the NMR spectrum in Fig. 4(b) and the value in Table 4]. A possible explanation for this will be discussed below.

**Rhodium**

The decrease in the rate of exchange with time in experiment Rh2 at 333 K and the low rate of reaction compared with that for Rh1 suggest that self-poisoning of the reaction was occurring, probably through the formation of more strongly adsorbed species which are less readily desorbed and more likely to undergo carbon—carbon bond rupture. Decreasing rates of exchange have been reported for the reaction of various hydrocarbons containing quaternary atoms at 423 K on Rh/silica, and the deceleration varied with the hydrocarbon. Rhodium is one of the most effective catalysts for hydrogenolysis and carbon—carbon bond rupture has been observed at 340 K with cyclopentane. Consequently, it is hardly surprising to find some evidence of poisoning of the exchange of methylcyclopentane at 333 K.

The product distribution for Rh2 showed a rather uniform distribution to the D₈ compound and then decreasing percentages up to D₁₁. Results for both Rh1 and Rh2 in Table 4 show that Rh is relatively inefficient for hindered side exchange and that the extent of methyl group exchange is dependent on temperature. The values in Table 5 show that turnover occurs to a lower extent on rhodium than on platinum at the same temperature. Analysis of the deuterium in the methyl group shows that 51% of the products from Rh2 were exchanged in the methyl group. This figure is slightly higher than the 37% from Pt2 and the 34% for Pd2 and may account for the rather uniform distribution of products up to D₈.

The NMR spectrum of the products from experiment Rh1 provided data on the relative extents of exchange in the six positions, given in Table 4, but was not sufficiently intense to give a reliable resolution of each resonance into the groupings identified for the other experiments, shown in Tables 2 and 3.

**Conclusions about Mechanisms**

**Initiation of Exchange**

Since open side exchange generally occurs to a greater extent than hindered side exchange, it is likely that the initial dissociation to form an adsorbed alkyl intermediate is slightly easier for positions I—III, than for positions IV and V. This suggests that the presence of the methyl group reduces the strength of adsorption of intermediates attached to the surface on the hindered side so that they are formed less readily.
Propagation of Exchange

The results, particularly the positions of maxima in the distribution of products from reactions on palladium, are consistent with the accepted main mechanism of multiple exchange as the interconversion between adsorbed alkyl and adsorbed alkene intermediates, the so-called $\alpha\beta$-process. The efficiency of this process varies with the metal in the order Pd > Pt > Rh.

Methyl Group Exchange

The results provide new evidence about the mechanism for the propagation of the exchange from the open side of the ring to the methyl group. This can take place by the general $\alpha\beta$-process but it requires the formation of an exocyclic alkene species involving a change in the orientation of the molecule on the surface. The evidence that substantial percentages of the products are not exchanged in the methyl group shows that the propagation to permit such exchange does not occur as readily as multiple exchange of ring hydrogen atoms. However, once the process starts, presumably involving the change of orientation, a rather efficient $\alpha\beta$-process allows extensive replacement of the methyl hydrogen atoms to take place. This feature of a high degree of exchange of the methyl group was observed over all three metals even though the fraction of the molecules undergoing methyl group reaction varied with the metal.

Turnover

In every case the chance of 'turnover' was greater for molecules which began exchange on the hindered side and lower for molecules initially exchanged on the open side, as shown by the values in Table 5. This fits with the idea that intermediates adsorbed on the hindered side are less strongly held and can more easily form the type of alkene responsible for turnover which must involve passage through a loosely held 'vertical' orientation. The chance of this reaction is enhanced by increase of temperature on all metals showing that additional activation energy is needed. The chance of turnover also depends on the metal and the order is Pd > Pt > Rh which is an indication that adsorbed alkene is least strongly held on palladium.

Minor Processes

Stepwise exchange, i.e. reversible formation of an adsorbed alkyl intermediate without further dissociation, makes some contribution, particularly at the lower temperature. This was obvious with experiment P11 but appreciable amounts of the D$_3$ compound, Table 1, were observed with Rh1 and Pd1 and also with Pt2. The NMR spectrum for Pd1 in Fig. 4(a) shows evidence of small peaks corresponding to singly exchanged deuterium atoms in positions II, III and IV.

All of the distributions showed that more D$_3$ than D$_2$ products were formed and in two cases, Rh2 and Pd2, there was evidence of a minor maximum for the D$_2$ compound. We believe these facts are indicative of some pairwise replacement of hydrogen atoms by a mechanism which involves exchange with a single molecule of D$_2$. Recent evidence of this type of reaction has been found for the exchange of cyclopentane over Ni/silica. The enhanced exchange in position IV observed with Pd2 may have occurred in this way but the shape of the resonance in Fig. 4(b) and the evidence in Table 5 of the same fraction of deuterium in positions IV and V in molecules exchanged on both sides indicate that there is more than pairwise exchange involved. We suggest that preferential formation of a (IV, IV)alkene occurs (some is desorbed as D$_2$ product but a higher fraction turns over to give products exchanged on both sides). Palladium not only is effective for multiple exchange but also is known to bring about reaction by several mechanisms, e.g. Schrage and Burwell$^9$ provided evidence of five processes for the exchange of cyclopentane on Pd/Al$_2$O$_3$.

Inspection of molecular models suggests that exchange in position V might be limited by steric hindrance. However, the results in Table 4 indicate that the relative exchange in this position is similar to that of position IV, except for the experiment Pd2 which has just been discussed.

Summary

The new evidence obtained by deuterium NMR analyses is helpful in confirming the accepted ideas about mechanisms of multiple exchange. In addition, it provides more insight into the process of turnover, the mode of exchange of the methyl group in methylecyclopentane and highlights the ways in which catalytic properties for exchange vary with the metal used.

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References


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