Probing the nature of molecular chemisorption using RAIRS

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Abstract

Reflection absorption infrared spectroscopy has now established itself as a powerful and versatile technique for monitoring molecular adsorption at defined single crystal metal surfaces. This paper discusses the success of the technique in providing a wide range of information, including the identification of hydrocarbon species and monitoring molecular adsorbate-induced surface reconstructions. The use of IR spectroscopy in determining the nature of chemisorbed species is discussed in the light of recent structural investigations questioning the validity of vibrational "fingerprints". Finally, the need for high resolution capability is demonstrated by new *intramolecularly* decoupled IR experiments which allow individual types of CH bonds in complex hydrocarbons to be identified.

Keywords: Atom–solid reactions; Carbon monoxide; Chemisorption; Copper; Infrared absorption spectroscopy; Low index single crystal surfaces; Nickel; Nitrogen oxides; Palladium; Solid–gas interfaces; Surface relaxation and reconstruction; Vibrations of adsorbed molecules

1. Introduction

Reflection absorption infrared spectroscopy (RAIRS) and electron energy loss spectroscopy (EELS) undoubtedly stand out as the most versatile techniques for obtaining vibrational information from adsorbed systems. Whereas 10 years ago, the primary concern for surface IR spectroscopists was to increase the sensitivity of the technique to allow adsorbates other than CO to be monitored on defined metal substrates, today experiments on a wide range of chemisorption systems are being conducted. The technical achievements in RAIRS have already been widely chronicled and reviewed [1–3]. Concurrently, there have been equally significant advances in the complementary technique of EELS [4–6]. As a result the demarcation between the two techniques, i.e. EELS providing high sensitivity over a larger spectral range but at low resolution (~ 40–50 cm^{-1}) and RAIRS providing good sensitivity with high resolution (0.5–4 cm^{-1}) but over a smaller spectral range, has now become blurred. Recent work, using synchrotron radiation sources, has opened up the low frequency region for the IR spectroscopist [7,8], while current EELS spectrometers are now routinely operating at ~ 20 cm^{-1} resolution, with recent advances in instrument design and resolution enhancement methods offering spectral resolution of ~ 8 cm^{-1} [4–6]. Finally, for RAIRS, even the operation of the strict dipole selection rule has been shown to break down with "dipole-forbidden" anti-absorption bands being observed for low frequency modes [7–9]! At present, the only difference that has survived is the inherent ability of the photon based RAIRS

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technique to operate under high pressure conditions [10,11] where the electron based spectroscopies cannot operate. Perhaps, the provocative question that can be posed is: for chemisorption on defined metal crystals under high vacuum conditions, what can RAIRS offer over and above the EELS technique with its new generation of spectrometers and resolution enhancement methods?

Apart from the relative technical merits of a particular vibrational technique, there now also exists a more important issue for all vibrational spectroscopists, namely what information does the vibrational spectrum provide about chemisorption? This issue has been brought to the fore by recent results obtained by photoelectron diffraction (PED), dynamical LEED and SEXAFS studies [12–16] which question some of the fundamental premises underlying the analysis of vibrational spectra.

It is impossible, in the space of this paper, to review all the advances and controversies that concern the technique of RAIRS. Hence, only selected topics have been chosen which demonstrate some of the difficulties and some of the interesting developments of this technique in understanding molecular chemisorption at metal surfaces. The recent advances in far-IR experiments are the topic of a separate contribution by Hirschmugl et al. in these Proceedings.

2. Adsorbate site symmetry analysis

The power of vibrational spectroscopy in providing information on the chemisorbed layer arises largely from the availability of a wide database of "group frequencies" that has accumulated from studies of "free" molecules, metal cluster compounds and supported catalysts. In particular, the vibrational frequencies of structurally determined cluster compounds provide a valuable reference for understanding adsorption at surfaces. The analysis of CO adsorption on metals is a prime example of such an approach, the local adsorption site being inferred directly from the frequency of the internal νC–O stretching vibration. Thus, three categories of adsorbed species can be identified, each exhibiting a νCO frequency in a particular range: ~ 2130–2000 cm^{-1} for on-top CO; ~ 2000–1880 cm^{-1} for two-
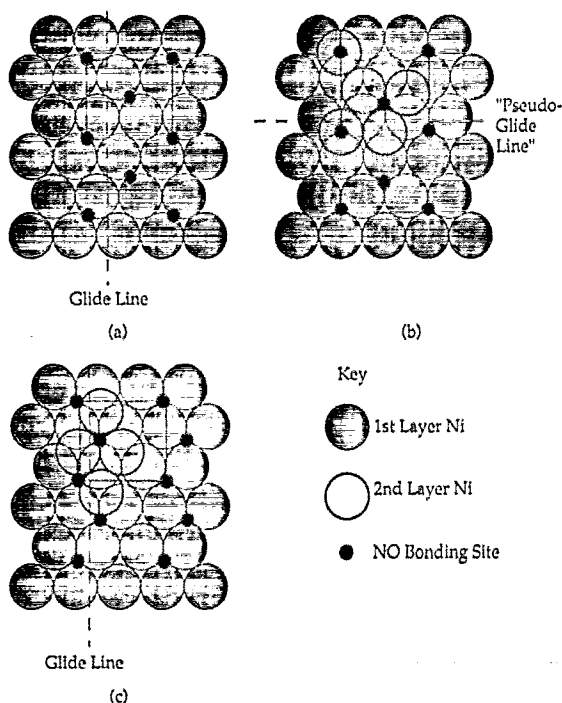

Fig. 1. Adlayer models proposed for the c(4×2)NO/Ni{111} structure; (a) The PED structure. (b) The LEED and SEXAFS structure and (c) the RAIRS structure. (With permission from Mapledoram et al. [14].)

fold bridging CO and 1880–1650 cm^{-1} for multiply coordinated CO [17]. A similar approach has also been extended by surface scientists to deduce the adsorption site of NO. It, therefore, was a matter of great interest when recent PED, LEED and SEXAFS studies [12–16] suggested that the accepted correlations between the frequency of the internal molecular vibration and adsorption site could no longer be regarded as safe. Two systems for which vibrational spectroscopy "failed" are summarised below.

2.1. c(4 × 2) NO / Ni{111}

IR data for NO/Ni{111}, corresponding to the ordered c(4 × 2) LEED structure at half monolayer coverage, show a single ν(NO) stretching band at 1581 cm^{-1} [18]. In keeping with the organometallic literature and the published analyses of other NO adsorption systems, the IR data was interpreted in terms of adsorption into two-fold bridge sites, Fig. 1c [14]. This assignment was subsequently questioned by PED studies [12] which concluded that
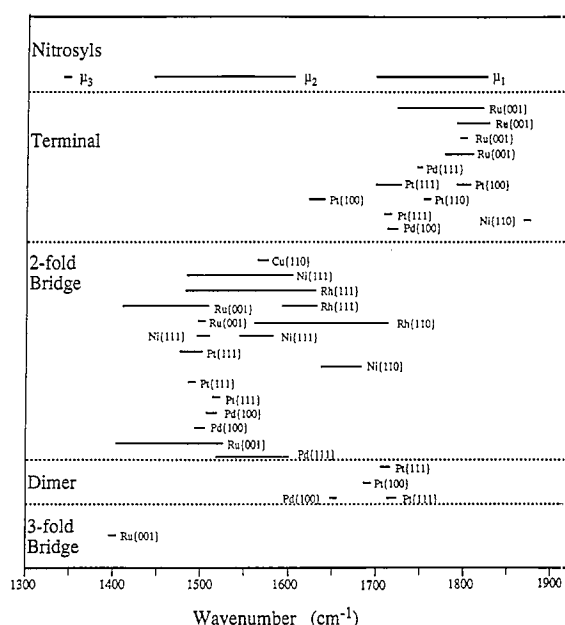
Fig. 2. Vibrational assignments offered for NO adsorbed on a range of transition metal surfaces [14].

adsorption of NO in the c(4 × 2) structure occurs solely in the fcc three-fold hollow sites, Fig. 1a. However, recent LEED studies [14] argue, on symmetry grounds, for an adlayer structure in which both the hcp and fcc three-fold hollows are occupied, Fig. 1b. This conclusion is also consistent with the SEX-AFS data on this system [13].

It is clear from the preceding discussion that the νNO frequency was not a reliable indicator of adsorption site. In fact, a brief review of the literature on adsorbed NO [19] shows an alarming variability in site assignment made by vibrational spectroscopists, Fig. 2, demonstrating the underlying weakness of the current reference framework. The difficulty of pigeonholing νNO frequencies to particular geometries can be traced directly to the electronic nature of NO, where the presence of an extra electron in the $2\pi^*$ level profoundly affects the chemistry of this molecule, making it both an electron acceptor and donor, more polarisable, able to coordinate in bent and linear configurations and amenable to dimerisation! Therefore, the vibrational frequency of adsorbed NO can be expected to vary widely, even when restricted to a particular coordination geometry, and it is reasonable to conclude that a

good frequency/geometry correlation cannot be attempted. Consequently, more detailed understanding of NO chemisorption will necessarily require a combination of techniques: structural techniques furnishing details of the adsorption site while vibrational spectroscopies, perhaps, exploiting the extreme sensitivity of the νNO stretch to follow subtle changes in metal–molecule and molecule–molecule interactions.

2.2. c(4 × 2) CO / Ni{111}

The difficulty of correlating νNO frequencies to adsorption sites can be rationalised in terms of the wide-ranging response of the molecule to its local environment. CO, on the other hand is a comparatively "well-behaved" molecule, the empty $2\pi^*$ antibonding orbital restricting its chemical versatility. It, therefore, came as a surprise when the very widely accepted carbonyl database was also brought into question for the c(4 × 2)CO/Ni{111} system. IR data for this system shows two bands at 1816 and 1831 cm^{-1} at low coverage, attributed to three-fold and two-fold coordinated CO respectively [20]. With increasing coverage only one band is observed which shifts from 1831 to 1905 cm^{-1} as the ordered c(4 × 2) structure is formed at a coverage of a half monolayer. This band is assigned to two-fold bridged CO in the c(4 × 2) structure. Subsequent PED [15], LEED [16] and SEXAFS [21] analyses of this system disagree with the vibrational interpretation and assign CO adsorption in the c(4 × 2) structure to hcp and fcc three-fold hollow sites, producing a structure similar to that proposed for the analogous NO adlayer, Fig. 1b.

This work clearly establishes the value of structural techniques like PED and LEED in identifying adsorption site geometries. However, in contrast to the situation for NO, it cannot be concluded that the correlation of carbonyl frequency to adsorption site has been seriously compromised. The IR data for the CO/Ni{111} system is actually compatible with three-fold adsorption; the νCO stretching frequencies of 1831 and 1816 cm^{-1} observed at low coverage lie well within the multiply coordinated range put forward by Sheppard and Nguyen [17]. As pointed out by Mapledoram et al. [16], the upshift in frequency of the 1831 cm^{-1} band to 1905 cm^{-1} and

the "intensity stealing" of the low frequency 1816 cm^{-1} band is entirely consistent with the occurrence of non-local phenomena such as dipole–dipole coupling and chemical shifts which have been widely documented and accepted by surface IR spectroscopists [1,3,22]. Perhaps, the primary lesson to be drawn from this system is that the assignment of adsorption sites cannot rely on frequencies established at any one coverage, but rather requires vibrational information obtained over a wide coverage range.

3. Molecular adsorbate induced surface reconstruction

The importance of interpreting infrared spectra in the context of data obtained over a wide coverage and temperature range is forcibly reinforced by the CO/Pd{110} system. RAIRS data [23,24] obtained at 300 K show a remarkable set of spectra, Fig. 3, starting with a single band at 1882 cm^{-1} at low coverages, progressing to a spectrum of incredible complexity at $\theta = 0.6$ where bands are observed over the entire 1800–2050 cm^{-1} range, culminating in a

single band at 2003 cm^{-1} at $\theta \sim 1$. Interestingly, LEED data show a (1 × 1) structure up to $\theta = 0.3$, a (4 × 2) structure over the coverage range $0.3 < \theta \leqslant 0.75$, and a sharp (2 × 1)p2mg structure at saturation monolayer coverage. The spectrum at $\theta = 0.6$ clearly defies any attempt to assign individual IR bands to particular adsorption sites! On the other hand, it holds vital clues to understanding this fascinating adsorption system.

In contrast to the behaviour at 300 K, adsorption at 180 K proceeds along more "conventional" lines with one or two band spectra observed over the entire coverage range up to a monolayer, Fig. 3. The associated LEED structures at low coverages are also different, passing through the sequence (2 × 1) and (4 × 1) before producing the (2 × 1)p2mg structure at $\theta = 1$, also observed at 300 K. The temperature behaviour of the system indicates that the IR behaviour at 300 K follows the thermodynamically favoured route. More interestingly, this data shows that though the low coverage ($\theta < 0.3$) and the saturation coverage structures could be formed at both 180 and 300 K, the formation of the intermediate phase over the coverage range $0.3 < \theta \leqslant 0.75$ is kinetically hindered at 180 K and can only form at
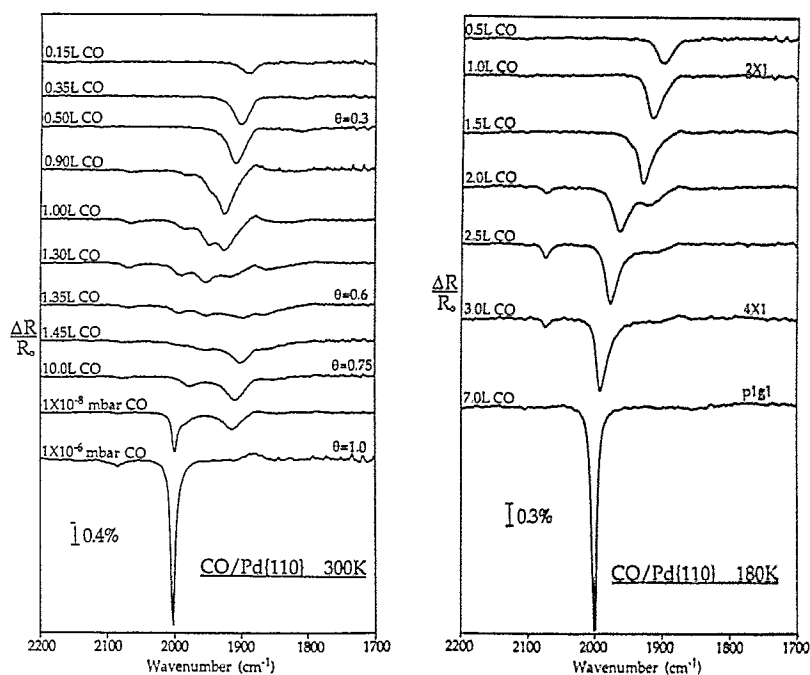

Fig. 3. RAIRS spectra observed for CO adsorption on Pd{110} at 300 and 180 K. Res = 2 cm^{-1}.

Table 1
The adsorption sequence followed by CO on Pd{110} at 300 K

Coverage	Surface structure	LEED
0–0.3	Bulk truncation Pd{110}-(1×1)	(1×1)
	↓ E_{act}	
0.3 < θ < 0.75	Bulk truncation Pd{110}-(1×1)	(4×2)
	+	
	Missing row Pd{110}-(1×2)	
0.75	Missing row Pd{110}-(1×2)	(4×2)
	↓ E_{act}	
1.0	Bulk truncation Pd{110}-(1×1)	(2×1)p2mg

temperatures > 250 K. The inescapable conclusion from this behaviour is that the structure formed at intermediate coverage needs to overcome a substantial barrier of formation, consistent with a reconstruction of the surface Pd layer. On this basis, the model outlined in Table 1 was proposed, involving initial adsorption of CO on the bulk truncation Pd{110} surface. However, once a critical local coverage is reached, the CO induces a missing row reconstruction of the Pd surface which is completed at θ = 0.75. Over the coverage range 0.3 < θ ⩽ 0.75, the bulk truncation and the missing row structures coexist, giving rise to the remarkably complex sequence of IR spectra observed in this regime, Fig. 3. Clearly, in this case, the internal νCO stretching vibration provides a valuable indicator of surface complexity. Additionally, isosteric heats of adsorption obtained using IR spectroscopy reveal that the reconstruction of Pd{110} is driven by the higher heat of adsorption of CO on the MR (1 × 2) Pd surface. Finally, increasing the coverage beyond 0.75 of a monolayer causes the surface reconstruction to be lifted and the (2 × 1)p2mg structure is formed on the bulk truncation Pd{110} surface.

The various aspects of the model suggested for this system have been verified by a number of IR experiments [23,24] and the presence of the missing row structure confirmed by LEED *I/V* studies [25]. Recently, FIM images of CO adsorbed on Pd particles have also provided direct support for a CO induced missing row reconstruction of these surfaces [26].

The use of coverage and temperature dependent IR studies in mapping out complex phase diagrams has also been demonstrated for the NO/Pd{110}

system, in which substantial (1 × 3) missing row reconstruction of the Pd surface is implicated [19]. For this study, the high resolution capability of RAIRS provided the only means of monitoring vibrational bands from two different surface species, separated by just a few cm^{-1}. Although, the analysis of the NO/Pd{110} system was necessarily complicated by the vagaries of the νNO stretching frequency and only tentative site assignments offered [19], this, nevertheless, did not hamper the broad understanding of the chemisorption system. This statement is equally true of the CO/Pd{110} system, however, in this case the band frequencies observed at low coverage can be attributed to adsorption in two-fold sites. In addition, the band observed at 2003 cm^{-1} for the saturation (2 × 1)p2mg adlayer can also be assigned to two-fold adsorption on the basis that it evolves smoothly from a lower coverage band observed at ∼ 1950 cm^{-1}. It, therefore, seems reasonable to conclude that the "singleton" frequency for the νCO vibration in the (2 × 1)p2mg structure lies well within the range expected for two-fold coordination, the final frequency of 2003 cm^{-1} representing considerable upshifting due to coupling and chemical shifts. Interestingly, this assignment has also recently come under scrutiny with LEED results [27] favouring an adlayer structure in which the CO's occupy on-top sites. This result signals a rather more significant failure for the carbonyl database, particularly in light of the analogous (2 × 1)p2mgCO/Ni{110} structure which gives rise to a νCO frequency of 1998 cm^{-1} [28] and is attributed to two-fold adsorption [29], thereby suggesting that two similar structures with similar νCO frequencies could still arise from different types of adsorbed species. However, the conclusions of the LEED analysis have recently been challenged. LDA calculations [30] show a strong preference for the two-fold bridge sites while very recent PED data [31] also favour a structure in which CO adsorption occurs in the two-fold bridging sites. The case continues.

4. Hydrocarbon adsorption at surfaces: the surface-cluster analogy

Vibrational spectroscopy has made an outstanding contribution in the study of hydrocarbon adsorption

[32] and the use of group frequencies to analyse data is manifest here, with spectral interpretation relying strongly on utilising model organometallic compounds whose structures have been well characterised by a range of techniques, including X-ray diffraction and NMR spectroscopy. Given the current re-examination of vibrational data from discrete clusters to describe chemisorption of CO and NO, it is equally relevant to consider whether the organometallic cluster provides a good reference framework for describing hydrocarbon adsorption on extended surfaces. It should be noted that, unlike studies on CO and NO, there has been no serious attempt to deduce adsorption sites of hydrocarbons from vibrational data. Instead, the database has simply been used to derive a chemical description of the surface ligand, i.e. hybridisation of C atoms, carbon–carbon bond orders, etc. The vibrational literature on hydrocarbon chemisorption at metal surfaces has been reviewed by Sheppard [33].

The identification of the ethylidyne species represents one of the successes of vibrational spectroscopy; the structure derived for this entity on Pt{111} relying heavily on the information provided by the EELS data [34] and subsequent confirmation from the crystallographically characterised [Co_3 $(CO)_9(u_3$-$CCH_3)$] cluster [35]. Dynamical LEED studies have verified the findings of the vibrational spectroscopist for this species [36]. It is also interesting to note that recent structural studies using NEXAFS [37] and PED [38,39] have confirmed the vibrational analysis of acetylene adsorption on Cu{111}, Pd{111} and Ni{111}. It, therefore, seems that the use of vibrational fingerprints from discrete metal clusters provides a good reference for describing hydrocarbon adsorption. Perhaps, a large measure of this success derives from the fact that analysis of spectra

from these compounds relies on "pattern recognition" based on the frequencies and relative intensities of a number of vibrational modes, rather than utilising just the one internal frequency as is the case for diatomics like CO and NO.

Although, EELS has, to date, made the major contribution in providing vibrational information on surface hydrocarbons, good quality, high resolution IR data are now increasingly becoming available, even for very weak absorbers. The adsorption of C_2H_4 on metals is a case in point and is briefly described below.

4.1. Low temperature ethylene adsorption on Ni{111} and Cu{110}

The adsorption of ethylene on metal surfaces can be understood in terms of the Dewar–Chatt–Duncanson (DCD) model [40], put forward to rationalise ethylene coordination in organometallic clusters. Essentially, the interaction is controlled by donation of electron density from the highest occupied molecular π level and backdonation from the metal into the empty π^* level. Both types of electron transfers increase the metal–molecule bond strength and weaken the molecular carbon–carbon bond. On the basis of this model, three extreme descriptions of adsorbed ethylene can be formulated, depicted as the di-σ, the metallocyclopropane and the π-adsorbed species [33,42], Fig. 4. The vibrational fingerprints for these species have been reviewed by Sheppard [33] and fall within three main patterns.

Fig. 5 displays the RAIRS spectrum associated with the (2 × 2) structure formed when ethylene is adsorbed on Ni{111} at 110 K. A fuller account of this work is provided elsewhere in these Proceedings [41]. The frequency of the νCH band at 2943 cm^{-1} confirms sp^3 hybridisation of the C atom and, by implication, the di-σ adsorbed species. In fact, the entire IR spectrum conforms well to the vibrational pattern exhibited by such a species and good correspondence is found with the model organometallic compound [$Os_2(CO)_8(u_2$-η_2-$C_2H_4)$] [43]. Simple application of group theory and the metal surface selection rule reveals that all the absorption bands observed arise from those vibrational modes that transform as the totally symmetric A_1 representation for a molecule adsorbed in C_{2v} symmetry at the
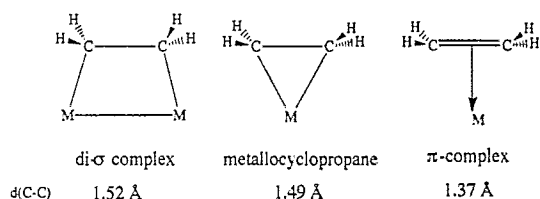

Fig. 4. The range of species formed by ethylene adsorption on metal surfaces [42]. The expected C=C bondlength is quoted for each case.

surface. This site symmetry is consistent with a complex adsorbed with the C–C bond parallel to the surface and a coplanar C_2M_2 skeleton.

Structural verification of the di-σ adsorbed species on Ni{111} has recently been provided by a PED study [44] which confirms the essential features of the geometry deduced from the RAIRS study. Although, the calculated PED bondlength of 1.60 Å ostensibly verifies the di-σ description, it is more difficult to extract a chemical description of the adsorbed ethylene from this information since the quoted error of ± 0.18 Å makes the data also compatible with the metallocyclopropane and π-adsorbed species.

Adsorption of ethylene on Cu{110} at 95 K stabilises a different type of surface complex [45] and the IR spectrum of this species is displayed in Fig. 6. For this species, the ν(CH) stretching vibration was not observed, however, the pattern of frequencies for the other modes follow that reported for the π-complex [33] and agree closely with the reported vibrations of the model Zeise's compound [42]. Again, the only modes that are observed are those that transform as the totally symmetric representation of a C_{2v} complex, arising from adsorption of the molecule with its C=C bond and the molecular plane parallel to the surface. This interpretation differs from that put forward by other groups who suggest a tilted
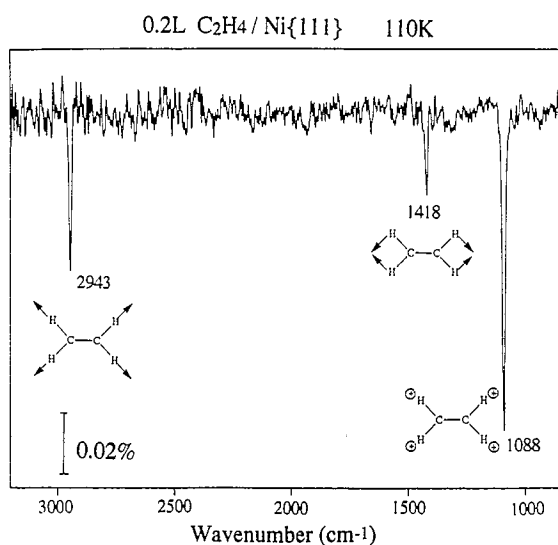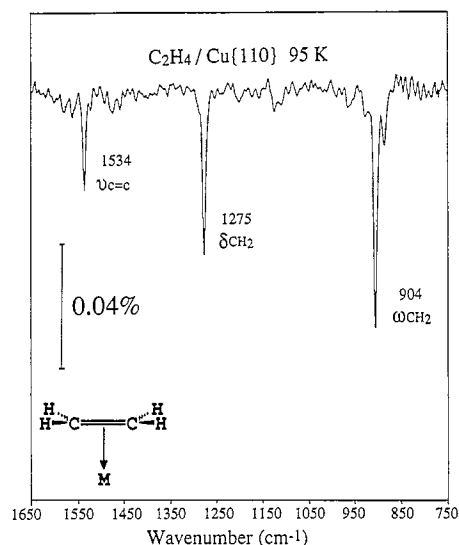

Fig. 6. RAIRS spectrum observed for the π-adsorbed ethylene species on Cu{110} at 95 K. Res = 4 cm^{-1}.

geometry [46,47]. In this respect, it is relevant to note that no modes indicative of a lower symmetry are observed and the larger than expected intensity of the coupled ν(C=C) and δ(CH)$_2$ vibrations at 1534 and 1275 cm^{-1} can be understood in terms of a strong π-interaction with this surface [45].

It would seem that the input of vibrational spectroscopy in understanding hydrocarbon adsorption is set to continue especially given the rich diversity of organometallic compounds available as suitable analogues for specific surface species. The particular contribution of high resolution data from RAIRS studies is also set to increase, with many systems requiring a working resolution of ~ 2 cm^{-1} to identify vibrations from separate modes in complex molecules. This high resolution capability becomes vital for certain specialised experiments of the type described below.

5. Intramolecularly decoupled infrared experiments

The use of *intermolecularly* decoupled IR experiments in which a dilute concentration of molecule distributed amongst an adlayer consisting of its isotope has been used widely in RAIRS experiments attempting to identify dipolar coupling effects [3,22].

Fig. 5. RAIRS spectrum observed for the (2×2) structure of di-σ ethylene on Ni{111} at 110 K. Res = 2 cm^{-1}.

The dilution of ^{12}CO amongst a ^{13}CO adlayer is possibly the most common example of this type of experiment. In contrast, *intramolecularly* decoupled experiments are rare. In a range of recent studies [45,48], we have investigated the potential of such experiments to reveal important aspects of hydrocarbon chemisorption.

The normal modes of vibrations of complex molecules can involve significant amplitude in a number of groups in the molecule; the νCH stretching vibrations of ethylene are a case in point, where the normal modes involve stretching of all the C–H groups, each mode describing a particular combination of in-phase and out-of-phase motions, leading to what is described as symmetric and antisymmetric $\nu(CH)_n$ stretches. However, complete decoupling of CH bonds can be achieved if all, but one, of the hydrogens is replaced by deuterium; the $\nu(CH)$ vibration collapsing from a normal mode description to an effective local oscillator description. McKean [49,50] has utilised this method to obtain the vibrational frequencies of the so-called "isolated CH" group in gas and liquid phase molecules, thus successfully identifying different types of CH bonds, often existing in compounds where nominally one might expect equivalence.

I have chosen the adsorption of C_6HD_{11} on Ni{111} to provide an illustration of the totally decoupled IR experiment [48]. Two types of CH groups can be identified in the stable chair conformation of cyclohexane: the axial CH and the equatorial CH, Fig. 7. Interestingly, liquid phase data [51] show these two groups are chemically distinct exhibiting isolated νCH vibrations of 2884 and 2915 cm^{-1}, respectively. This information is effectively scrambled in the C_6H_{12} molecule, where the normal modes of vibration involve coupled motions of both the axial and the equatorial groups [52].
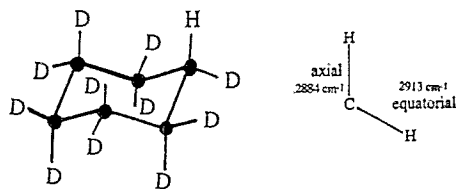

Fig. 7. Chair conformation of cyclohexane (C_6HD_{11}), possessing an isolated CH group, which can be positioned either axially or equatorially, giving rise to a different stretching frequency.
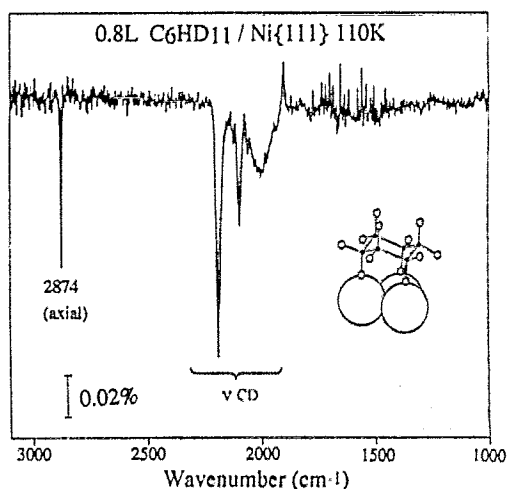

Fig. 8. RAIRS spectrum of a submonolayer of C_6HD_{11} adsorbed on Ni{111} at 110 K. The νCH and νCD regions are indicated. (Negative bands in the region below 2000 cm^{-1} arise from displaced CO on the surface and miscancellation of atmospheric water bands.) Res = 2 cm^{-1}.

Fig. 8 displays the IR spectrum obtained for a submonolayer of C_6HD_{11} adsorbed on Ni{111} at 110 K. The molecule adsorbs molecularly under these conditions [53]; the $\nu(CD)$ vibrations confirm this. The most interesting point about this spectrum is that the νCH region exhibits a single, sharp band at 2874 cm^{-1}, in stark contrast to the νCD region where a range of coupled νCD vibrations are seen. More importantly, the frequency of the νCH band identifies it as arising from the axial CH bond stretch. There is no sign of the equatorial νCH stretch, despite the fact that this vibration possesses the greater intensity in the "free" molecule [51]. The obvious conclusion to be drawn from this is that the molecule is adsorbed so that the axial bonds are directed largely perpendicular to the surface and the equatorial bonds largely parallel, i.e. the geometry depicted in Fig. 8, with the carbon skeleton parallel to the surface. Interestingly, increased coverage experiments show that this orientation is not strictly adhered to in the second layer and the equatorial CH stretch becomes visible [48]. Whereas, the monolayer geometry has been deduced from C_6H_{12} studies by consideration of all the modes of vibration [52,53], the experiment with C_6HD_{11} allows this information to be readily discerned. Additionally, the loss of parallel orientation with increasing coverage was not obvious from the C_6H_{12} experiment [48]. The pres-

ence of a single band in the $\nu(CH)$ axial region also confirms the equivalence of the upward-pointing axial groups, consistent with C_{3v} geometry. This equivalence is, for example, broken when adsorption is carried out on an oxygen-doped Ni{111} surface, where three different types of axial CHs are discerned, separated in frequency by just a few cm^{-1} [48]. These deductions are also more difficult to make for the coupled C_6H_{12} species [52–54]. It should be noted that the effective $\frac{1}{12}$th dilution of the CH concentration stops us from detecting the broad, "softened" mode seen for the C_6H_{12} species. In conclusion, these first experiments on totally intramolecularly decoupled adsorbates promise to provide rich information, not only on adsorbate geometries, but on detailed chemical perturbations and related reactivity.

6. Conclusions

This article started by questioning the future role that RAIRS might play in investigating molecular chemisorption on defined surfaces, given the recent advances in the resolution capability of the EELS technique. It is clear from the discussion that followed that a very significant role remains for the RAIRS technique which is able to routinely operate at spectral resolution of 2 cm^{-1} or better. For example, the recent controversies in adsorbate site assignments demonstrates the need to obtain detailed frequency/coverage information while high resolution IR information in identifying temperature dependent behaviour underpinned the detection of molecular adsorbate induced surface reconstructions. Finally, increases in the sensitivity of the RAIRS technique has allowed routine monitoring of hydrocarbons to be conducted and, importantly, will play a leading role in allowing new types of experiments, such as the intramolecularly decoupled experiments described here, to be carried out. The need for high resolution (routinely 0.5–1 cm^{-1}) in this type work is vital.

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