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The reliability of vibrational spectroscopy as a means of identification of the structures of chemisorbed species on metal surfaces: the cases of CO, NO and C_2 hydrocarbon surface species

Norman Sheppard[a,*], Carlos De La Cruz[b]

[a] *School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK*
[b] *Departamento de Quimica, Facultad de Ciencias, Laboratorio de Espectroscopia Molecular y Atómica, Universidad del Zulia, Maracaibo, Venezuela*

Abstract

A review of the literature shows that vibrational spectroscopy has been extremely successful in anticipating the structures of C_2 chemisorbed species that are later evaluated by the more direct methods of photoelectron diffraction (PED), low energy electron diffraction (LEED) and scanning tunnelling microscopy (STM).

More difficulties have attended these comparison procedures as applied to the spectra of adsorbed CO and NO, where the diffraction methods have shown that on (1 1 1) planes the 3-fold bridged species on 'hollow' sites occupy a wider range of coverages than had been anticipated spectroscopically. Exceptional coverage dependence of the positions of the νCO and νNO absorption bands leads to overlap of the characteristic wavenumber ranges for the 2-fold bridge and 3-fold bridged surface species except at low coverages. The high coverage-dependence of these spectra is associated with the exceptionally high intensity of these absorptions leading to vibrational dipolar coupling and to sensitivity to static electronic interactions with neighbouring adsorbed molecules. Such factors are minimal in the spectra of the C_2 species.

It is concluded that the 3-fold bridged CO surface species has an extended wavenumber range 1950–1800 cm^{-1} (high to low coverage), which overlaps at moderate coverages with that of the 2-fold species between 2000 and 1870 cm^{-1}. An exhaustive literature survey has yielded improved νNO wavenumber ranges for adsorbed NO species at low coverages, namely M–NO linear (on-top site), 1800–1720 cm^{-1}; M–NO bent, 1700–1620 cm^{-1}; 2-fold bridge, 1570–1500 cm^{-1}; 3-fold bridge (hollow site) 1470–1380 cm^{-1}.

Keywords: Vibrational spectroscopy; Chemisorption; Hydrocarbon surface

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1. Introduction

Vibrational spectroscopy was the first physical method used to deduce the structures of chemisorbed complexes on metal surfaces and, because of its relative experimental ease, it remains one of the most widely used. In recent years the results of the more direct, but experimentally more demanding, photoelectron diffraction (PED) and low energy electron diffraction (LEED) methods have reached conclusions at variance with those derived previously from vibrational spectroscopy for adsorbed NO [1,2], and CO [3,4]. The disagreements concern principally the lack of spectroscopic identification of 3-fold bridged adsorbed species at higher coverages on hollow sites

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[*] Corresponding author.
E-mail address: n.sheppard@uea.ac.uk (N. Sheppard).

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of (1 1 1) surfaces. These few cases, to be discussed below, have unfortunately led to unwarranted concern about the general reliability of the vibrational spectroscopic method for adsorbate structure determination.

The present paper relates the above anomalies to an underestimation of the coverage dependence of spectra from the 3-fold bridged species, which in turn had led to an unrealised overlapping of the regions characteristic of 2- and 3-fold bridged species. It is shown that the spectroscopic method, whereby the spectra of the adsorbed species are compared with those of metal coordination or cluster compounds of known structures, usually determined by X-ray crystallography, remains valid for the low-coverage spectra of CO and NO and for identifying the linear (on-top) species. Coverage-dependent band-region overlaps are most likely to occur when the absorptions concerned are of exceptionally high intensity, as is the case with the νNO and νCO bond-stretching modes. Where this is not the case, as exemplified in the spectra from C_2 hydrocarbon surface species, the spectroscopic method is shown to be highly successful at predicting the structures later identified by diffraction methods.

In the course of the discussion, a preliminary account is given of a recent improved analysis of the spectroscopic ranges which are characteristic of the different types of adsorbed species from NO chemisorption.

2. Factors affecting the positions of vibrational bands from the same type of adsorbed species: the case of adsorbed CO

For this purpose, the results summarised in reviews by Sheppard and Nguyen [5] are made use of for spectra from the bond-stretching mode of vibration of CO (symbolised by νCO) adsorbed on finely divided or single-crystal metal surfaces and by De La Cruz and Sheppard [6] of CO as a ligand in metal coordination and cluster compounds.

2.1. Metal variability

This is best explored by considering the mean νCO values in cm^{-1} (taking into account infrared and Raman data and the appropriate vibrational degeneracies) from the carbonyls of different metals, M: metal. The results are [6]:

$$M(CO)_4: \quad Ni(2077) \quad Pd(2080) \quad Pt(2067)$$

$$M(CO)_5: \quad Fe(2025) \quad Ru(2035) \quad Os(2030)$$

giving a mean value of ca. 2050 cm^{-1} with a variability of $\pm 30\ cm^{-1}$. This is for the linear MCO group which, when occurring on a surface, is frequently described as the ‘on-top’ species.

There are fewer examples of 2-fold bridged species, M_2CO, in all-carbonyl coordination compounds but the mean value is ca. 1855 cm^{-1}.

2.2. Degree of coordinative unsaturation of the adsorption site

For an f.c.c. metal, a metal atom away from the surface has full coordinative saturation by 12 nearest neighbours. Related to this, top-surface atoms have coordination unsaturations of $\frac{1}{4}$ for (1 1 1), $\frac{1}{3}$ for (1 0 0) and $\frac{1}{2}$ for (1 1 0) surfaces. Similar considerations apply to edge and corner atoms of metal crystallites or step and kink sites on non-flat single-crystal surfaces. Greenler and colleagues [7,8] have studied these two cases for the surfaces of Pt. From the study of finely divided Pt crystallites of different sizes they deduced values of 2081, 2063, and 2070 cm^{-1} for the νCO frequencies on face, edge and corner sites, respectively. From (5 5 3) and (4 3 2) single-crystal surfaces they derived values of 2074, 2065 and 2060 cm^{-1} for isolated (low coverage) CO molecules on terrace, step and kink sites, respectively. It is concluded that these differences fall well within the general range for identifying on-top CO species. These are the variabilities earlier envisioned by Blyholder [9] which turned out to be very limited in magnitude.

2.3. The electronic effects of CO-ligands or co-adsorbates

In an exhaustive study of data from linear-CO liganded to metal coordination and cluster compounds of platinum [6], it was concluded that the following approximate, and approximately additive, effects on νCO (cm^{-1}) occur as a result of a change in the charge on the metal atom or the presence of electron-withdrawing or electron-donating ligands attached to the same metal atom. These band shifts (cm^{-1}) are relative to νCO in uncharged coordination compounds with all-CO ligands:

Unit positive charge per metal atom	+90
Strongly electron-withdrawing co-ligands, e.g. Cl or Br	+50
Unit negative charge per metal atom	−140
Strongly electron-donating co-ligands (e.g. PR_3, R: alkyl or aryl; cyclopentadienes)	−50 to −70

Effects of this type also occur in the spectra of linear-CO adsorbed on surfaces as a result of the presence of such types of co-adsorbates, e.g. electron-withdrawing O, Cl, etc. causing positive wavenumber shifts in νCO [10], or electron-donating NH_3, K, etc. causing negative ones [11,12]. These effects can also be large, varying from tens to two hundred wavenumbers, the latter because of the effects of multiple co-adsorbate neighbours, particularly for the highly electron-donating alkali-metal co-adsorbates [12]. When CO is adsorbed on an electrode, changes in νCO also occur in the expected directions when the electrode potential is increased or decreased [13].

2.4. The degree of surface coverage

In the absence of the effects of strongly electron-donating or electron-withdrawing co-adsorbates, Sheppard and Nguyen [5] and De La Cruz and Sheppard [6] deduced the following approximate values that can be expected to occur on metal surfaces:

Linear (on-top sites)	2130–2050–(2000) cm^{-1}
2-fold bridged	(2000)–1980–1870 cm^{-1}
3-fold bridged species (on hollow sites)	1880[a]–1800 cm^{-1}
2-fold long bridges[b]	ca. 1700 cm^{-1} (few examples)

[a] This value requires modification (see below).

[b] $\sqrt{2}$ times the in-contact metal internuclear distance can occur between adjacent rows of a (1 1 0) surface or across the diagonal of a square unit cell of a (1 0 0) surface; the much lower value for the long bridge corresponds to a wider MCM angle appropriate to sp^2 hybridisation. Within the above ranges, the high wavenumbers correspond to high coverages and vice versa. The values in brackets are for (1 1 0) surfaces; the others are for 'flat' (1 1 1) or (1 0 0) surfaces.

It is well established that there is a very substantial additional effect, not normally found in the spectra of coordination complexes, caused by the parallel orientation of co-adsorbed CO molecules on surfaces associated with the fact that this adsorbate (like NO to be considered below) has intrinsically a very high dipole change associated with its νCO-stretching mode. This leads, through resonant vibrational dipolar interaction between adjacent CO groups, to a considerable range of wavenumbers for the system of coupled νCO vibrations but with virtually all the intensity concentrated in the highest frequency mode in which all the dipole changes occur in unison [14,15].

Additional to the vibrational dipole coupling, a change in the number of neighbouring adsorbate molecules with respect to a given CO molecule can affect the νCO wavenumber through changes in electron density at the adsorption site, or by mutual polarisation. This 'static' or 'chemical' effect can in individual cases be similar in magnitude to that from dipolar coupling but can be in the same or opposite direction [15]. The two effects can be experimentally separated because dipolar contributions can be largely annulled by the isolation of a ^{12}CO adsorbate within a majority of ^{13}CO molecules. The latter have different values for νCO wavenumbers, thereby reducing much the resonance coupling [16,65]. The νCO absorptions are sufficiently strong that there is usually little difficulty in measuring the absorption of the 'diluted' ^{12}CO.

A third coverage-dependent effect on spectra, with which we are not concerned in our consideration of adsorption on (1 1 1) surfaces, is the restoration of reconstructed bare metal surfaces to their 'normal' configurations as a result of adsorption processes [17].

The dipolar coupling and chemical effects are manifest in coverage-dependent spectra of CO from the same type of surface species or sites on finely divided or single-crystal metals. The above ranges allocated to different species were chosen at a time when relatively few spectra were available on single-crystal surfaces. The assignments for the 3- and 2-fold bridged species were supported by coverage-dependent reflection–absorption infrared spectra (RAIRS) of CO on the single-crystal surfaces of Pd(1 1 1) and Pd(1 0 0) that were obtained by Bradshaw and Hoffmann [18]. The spectra on Pd(1 1 1) at 300 K commenced at ca. 1820 cm^{-1} at low coverage and split into two overlapping bands near 1850 cm^{-1}, close to one-third surface coverage, where a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface phase is found by LEED, leading to a replacement absorption near 1890 cm^{-1}. The 1880 cm^{-1} was, therefore, taken to be the upper-limit coverage by the 3-fold bridged species on this surface. The new set of absorptions continued to increase in wavenumber to higher coverage culminating at ca. 1945 cm^{-1} in a $c(4 \times 2)$ half-coverage surface array. This second set of adsorptions was presumed to be from the 2-fold bridged species. On the (1 1 1) surface, there are three sites available for 2-fold bridging compared with two for 3-fold bridging within the f.c.c. metal unit cell, so it seemed reasonable that the 2-fold species might take over at high coverage. Bradshaw and Hoffmann's [18] coverage-dependent CO spectra on Pd(1 0 0), where 3-fold sites are not present, gave one coverage-dependent set of absorptions between 1890 and 1930 cm^{-1} and another between 1950 and ca. 1985 cm^{-1}, both attributed to 2-fold bridged complexes, the latter in 'compressed' surface structures. There have been no claims to distinguish spectroscopically between the f.c.c. and h.c.p. 3-fold sites by vibrational spectroscopy.

2.5. Criticisms of the vibrational spectroscopic correlations for the 3-fold species based on PED and LEED

LEED patterns give particularly readily information about the unit cell size and orientation of the surface array, but the more difficult multi-scattering analyses based on likely possible structures are usually needed to deduce which alternative types of site are involved. Energy (and hence wavelength) scanning is used to determine adsorbent/adsorbate layer separations in the direction perpendicular to the surface.

The scanned energy PED technique has an additional capability over LEED that, like vibrational spectroscopy, it is local-site based with the signals originating in diffraction of photoelectrons coming, in this case, from the C or O atoms within the surface complex. Particularly when the site-symmetry is high, the latter can be deduced readily from a semi-quantitative 'projection' method; such qualitative results form the preliminary basis for multi-scattering searches for fits to the full experimental data based on likely alternative structural possibilities [19]. When the symmetry of the surface complex is lower than that of the bare metal surface the coexistence of differently oriented domains can make the interpretation of preliminary projection analysis more difficult. PED is easier to interpret when the metal surface is from first transition period elements such as Ni or Cu. For second transition period elements, such as Pd, the resolution of the PED signals from adjacent metal Auger features can be difficult. For adsorption on a (1 1 1) Ni surface the PED projection method can detect a 3-fold CO adsorption site with ease.

The interpretation of CO vibrational spectra on (1 1 1) surfaces, namely that spectra at low coverage are from 3-fold adsorbed species and that these are replaced by 2-fold bridged species where spectroscopic transitions occur between coverage-dependent band sequences in the lower 1880s, became widely accepted and was applied to other cases such as Ni(1 1 1). In that case, Surnev et al. [20] showed that band-sequence transitions occurred as follows near the surface coverages, θ, given in brackets: 1820–1830 cm^{-1} (0.03); 1855 to ca. 1870 cm^{-1} (0.3); and 1887–1902 cm^{-1} (0.5). The first of these transitions was assumed to represent the 3 to 2-fold transition in terms of surface species. However, it is now accepted that the PED technique has demonstrated that even at $\theta = 0.5$, where a well-defined $c(4 \times 2)$ surface array is formed (1902 cm^{-1}), the surface complex still retains the symmetry of the 3-fold species [3]. More recently, the same conclusion has been reached for the $c(4 \times 2)$ phase on Pd(1 1 1) by PED [21]. For this surface 3-fold sites were also confirmed, as expected from spectroscopy (1840 cm^{-1}), for the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$, phase at one-third coverage. This research was carried out because a similar conclusion had earlier been reached by PED for the c(4 × 2), $\theta = 0.5$, phase for NO on Ni(1 1 1) [1,22] (see below).

What is clear from these diffraction-based findings for CO adsorption is that a frequency change of several tens of wavenumbers from one sequence of coverage-dependent absorptions to another should not necessarily, as had frequently been assumed, be attributed to a change of surface species [1,3,22]. Such an observed increase in wavenumbers may alternatively be a reflection of the increased dipolar coupling or chemical effects that occur when one adsorbate surface lattice phase is replaced by another at higher coverage. If a change in species is additionally involved, the extent of change in wavenumber might be more pronounced. Since the early work described above for CO on Pd the resolution of RAIRS has been much improved through the use of Fourier transform methods [23]. A result is that frequently more such phase-to-phase spectroscopic transitions can be observed that can be related to species change.

Since the PED papers for CO and NO on Ni(1 1 1), several LEED papers concerned with CO adsorption on (1 1 1) metal single-crystal faces have also pointed to the spectroscopy-based miss-assignments to 2-fold rather than to 3-fold sites at higher coverages [4,24]. These include the (2 × 2)-3CO phase from CO on Rh(1 1 1) which shows vibrational electron energy-loss spectroscopy (VEELS) absorptions at 1870 and 2070 cm^{-1} that are now attributed to 3-fold (instead of 2-fold [25]) and linear (on-top) species, respectively. However a LEED-based claim for a change of assignment from the spectroscopically suggested bridged to a linear site for CO at full (2 × 1) *p2mg* coverage on Pd(1 1 0) [26] has not been sustained [27]. Even at the highest coverage for the 2-fold species there is so little overlap with the wavenumber range for the linear species that the spectroscopic assignments remain decisive in such cases on coverage criteria. In a fine paper, which delineates the full dispersion ranges for the various modes of CO on Ni(1 1 0) at the (2 × 1) *p2mg* coverage, by the use of on- and off-specular VEELS [28], it seems that nevertheless the theory-guided site assignment proposed should also be changed at this high coverage from on-top to 2-fold bridged for the absorption at 1984 cm^{-1}.

A case which would benefit from PED or LEED reinvestigation is that of the c(4 × 2) phase for CO on Pt(1 1 1) which has been studied by VEELS and RAIRS and showed two bands at 1850 and 2100 cm^{-1} attributed to 2-fold bridged and linear species [29,30]. The former band now might be from the 3-fold bridged species, as would be consistent with its wavenumber.

The revised low- to high-coverage spectroscopic range for the 3-fold site for adsorbed CO is now from 1800 to ca. 1950 cm^{-1}. The upper limit of this range is based on high-coverage absorptions attributed to (1 1 1) facets in spectra from finely divided Ni and Pd catalysts (see Fig. 11, p. 142 of Ref. [5]). It is also satisfactory that the revised range is comparable in extent to that found for the 2-fold bridge site. It is seen that the single correction that was needed to the earlier spectroscopic assignments was a recognition that coverage-dependent dipolar coupling or static chemical effects within the spectra from the 3-fold species on the (1 1 1) surfaces is sufficiently great to lead to an overlap with the 2-fold bridged range at coverages greater than about one-third. At the lowest coverages there is no reason to doubt the validity of the original spectroscopic distinctions between the different surface complexes formed by CO that are based on spectroscopic data from metal coordination and cluster compounds.

3. Vibrational spectroscopic assignments for NO on metal surfaces

Unlike the case of CO discussed above, there has as yet been few systematic analyses of vibrational (mostly infrared) data for νNO from coordination or cluster compounds for the purpose of assigning structures to adsorbed species (see, e.g. [31,32]). Such assignments for adsorbed species have mainly used particular examples from the literature for guidance and taken into account the general expectation that the wavenumber sequence is likely (as for CO) to be linear (on-top) > 2-fold bridged > 3-fold bridged (hollow) sites. There is an additional complication with NO, in comparison with CO, in that it has an extra uncoupled electron and a molecule singly bonded to metal can have a linear or bent configuration.

One of us has recently undertaken a systematic study of spectroscopic data from NO-containing coordination and cluster compounds, to be reported in detail elsewhere [33], and we outline here the preliminary conclusions. Although there are many data on NO complexes in the literature, the task of analysis has proved to be much more difficult than in the CO case because the great majority of the compounds involve co-ligands which are highly electron attracting or donating. Furthermore, it turned out from the many data for linear NO-ligands that there is considerably more variability in relation to the metal involved than is the case for CO. These two factors lead to wider wavenumber ranges having to be assigned for the different surface species. Our preliminary conclusions for the νNO ranges, after approximate corrections have been made for the effects of electron-withdrawing or -donating co-ligands, are as follows:

M–NO linear (on-top)	1800–1720 cm^{-1} [a]
M–NO bent	1700–1620 cm^{-1}
2-fold bridged (short or long)	1570–1500 cm^{-1}
3-fold bridged (hollow)	1470–1380 cm^{-1}

[a] Values between 1900 and 1800 cm^{-1} are found when electron-withdrawing co-adsorbates, such as O, are present [1,34].

The above ranges refer to low-coverage situations. When taking into account the usual increases in wavenumbers with surface coverage, and the presence of the additional bent species which absorbs between the ranges for the 2-fold bridge and the linear on-top species, more overlaps than in the CO case are likely between the different ranges at higher coverages. However, useful distinctions can still be expected to be made in low-coverage situations in general, and in the highest wavenumber range at high coverage.

Erley [35] was the first to study the adsorption of NO on Ni(1 1 1) at 85 K using the high resolution of RAIRS. At low coverage, he observed two close-lying absorptions at ca. 1460 and 1475 cm^{-1} which blended together to form an absorption increasing in coverage to 1513 cm^{-1}. Between 1.2 and 1.25 L a new absorption was formed at 1543 cm^{-1} which grew in intensity at the expense of the 1513 cm^{-1} absorption and moved to 1581 cm^{-1} for saturation at 2.4 L with a c(4 × 2) array and $\theta = 0.5$. He attributed the 1460–1513 and 1543–1581 cm^{-1} absorption sequences to different adsorbed species. However, Asensio et al. [1] choose this system for first study by PED and showed firmly that both absorption sequences were from 3-fold species. This assignment agrees with the above new spectroscopic expectations at low coverage and once again, as with c(4 × 2) CO on Ni(1 1 1), leads to the conclusion that the second sequence arises from the greater dipolar coupling or chemical shifts in the higher coverage c(4 × 2) phase. Later LEED studies, in conjunction with the PED results, have reached general agreement that (as also for CO/Pd(1 1 1) [21]) the c(4×2) surface array involves equal numbers of NO molecules in f.c.c. and h.c.p. sites in parallel zigzag chains with gaps in between [22]. Taking into account the non-equivalence of the f.c.c. and h.c.p. sites the primitive lattice, of type *p1m1*, is described as 2NO-(2 × 2) rectangular; if the difference between the f.c.c. and h.c.p. sites can be disregarded the lattice is effectively of type p2mg.

NO on Pt(1 1 1) at 95 K has also been studied using RAIRS by Hayden [36], who found a sequence 1476–1494 cm^{-1} replaced at higher coverages by another from 1700 to 1725 cm^{-1}. The former sequence is as now as expected for the 3-fold species (originally suggested to be the 2-fold bridged). The latter, greatly separated from the former and related to a p(2 × 2) lattice, is clearly from the on-top species as originally assigned by Hayden. He also did an isotopic dilution experiment which separated the dipolar and chemical contributions to the band sequences for the two species.

NO on Pd(1 1 1) at 100 K has been studied by the lower resolution VEELS method [37–39]. It shows a 1535–1600 cm^{-1} sequence which at high coverage shares intensity with an absorption at 1750 cm^{-1}. The latter is clearly from an on-top species, as in the Pt case. As the low-coverage spectra are consistently found to commence above 1500 cm^{-1}, it is possible that this is from a 2-fold bridge rather than a 3-fold one, but the low resolution of VEELS has to be borne in mind. This case requires further investigation.

Considerable attention has recently been given to LEED [40] and PED [41] studies of NO adsorbed on Rh(1 1 1) to give a revised structural assignment of on-top and 3-fold sites for the 3NO-(2 × 2) lattice. At this high coverage this is now agreement with the principal VEELS absorptions at 1840 and 1513 cm^{-1} observed at 250 K with the (2 × 2) lattice ([42], the value of 1513 cm^{-1} is consistent with a 3-fold site at higher coverage), but an additional weaker band at 1600 cm^{-1} suggests that not all the NO molecules have formed the regular array. At lower coverages, in the absence of the linear species, a band sequence from 1480 to 1630 cm^{-1} starts in the region now attributed to the 3-fold species [43].

The problems of overlapping wavenumber ranges for different surface species that have been encountered in the cases of CO and NO might occur with other ligands, such as NN and NCO surface species, which also have exceptionally strong intensities. Such problems are not expected to occur with the spectra of most adsorbates, such as those of the adsorbed C_2 hydrocarbon species to be considered below.

4. The vibrational spectra of C_2 hydrocarbons on metal surfaces

Another wide area of study has been the vibrational spectra of surface species derived from the chemisorption of ethene or ethyne on single-crystal metal surfaces. Once again in this area PED or LEED data are becoming increasingly available — very recently supplemented by the identification of adsorption sites and orientations by scanning tunnelling microscopy (STM) [44,45] — to provide more direct structural conclusions for comparison purposes. As demonstrated below, in general very satisfactory agreements have been reached with the earlier spectroscopic conclusions. The strengths of the absorptions from such hydrocarbon species are very much less than those from νCO or νNO so that wavenumber variations with coverage from the same species has not been an issue.

The spectra from these polyatomic adsorbates are necessarily more complex with absorption bands that extend over the whole wavenumber range. There were initially substantial difficulties in interpreting the several species spectra from ethene on finely divided catalysts until, by comparison with the later-available single-species VEEL spectra on metal single crystals, it was realised that the metal-surface selection rule (MSSR) applied effectively also to the chemisorbed species on metal particles. This story has been told elsewhere [46,47].

On flat metal surfaces, the same dipolar mechanism applies to the excitation of infrared spectra and to on-specular VEEL spectra. The MSSR requires that only those vibrations resulting in dipole changes perpendicular to the metal surface are allowed. These are the completely symmetrical vibrational modes of the surface complex. The MSSR provides an important means of distinguishing between species with different expected orientations with respect to the surface. A second impact mechanism in VEELS allows the remaining modes to occur but usually in the form of the much weaker features observed in spectra obtained more readily in directions away from the specular direction. There are also impact selection rules relating to the symmetry species of vibrational modes of the surface complex with respect to the plane of incidence of the electrons.

The general procedure for analysing the spectra of polyatomic adsorbates is to look for repetitive patterns amongst the collected spectra, taking into account band positions and intensities, on the assumption that each pattern corresponds to a different type of adsorbed species. For hydrocarbons, it is of value to do this for both the normal and perdeuterated species. Within a particular recognisable pattern there will, of course, be considerable variations in band positions depending, e.g. on the metal or crystal face involved.

Likely group-characteristic features within a particular spectroscopic pattern are then used to narrow down the possibilities for the structure of the adsorbed species. The spectra are then compared with the spectra of ligands of similar structures usually available in the literature from metal coordination and cluster compounds. In making such a comparison, the effects of the MSSR on the relative intensities amongst the absorptions of the adsorbate have to be taken into account. Also the other ligands present in the model compounds are best chosen to be, like CO, relatively neutral in terms of donating or withdrawing electrons from the metal atoms. Despite the uncertainties in this procedure, convincing identifications of the structures of the adsorbed species have been obtained in many cases.

Table 1 summarises the structural conclusions that have been reached by this means for the principal species resulting from the chemisorption of ethene (ethylene) or ethyne (acetylene) on metal single-crystal surfaces. The majority of the identifications were initially made from VEEL spectra and these were visually compared in a review [46] that can be

Table 1
A comparison of spectroscopic and diffraction-based structural assignments for chemisorbed species from C_2H_4 and C_2H_2[a]

Vibrational spectroscopy	Structural type	Diffraction or STM
C_2H_4 (low temperature)		
Type I[b]	Di-σ[c]	
Ni(1 1 1), Ni(1 1 0), Ni(1 0 0)[d]		Ni(1 1 1)[PED][e]
Fe(1 1 0), Ru(0 0 1)[b], Pt(1 0 0)		Ni(1 1 0)[PED, STM][f]
Pt(1 1 1)		Pt(1 1 1)[DLEED][g]
Type II[b]	'π-Complex'	
Pd(1 1 1), Pd(1 0 0)[h], Pd(1 1 0)		Pd(1 1 0)[STM][i]
Cu(1 0 0), Cu(1 1 0)[j], Cu(1 1 1)		Cu(1 1 0)[PED, STM][j]
Ag(1 0 0)		
C_2H_4 (room temperature)		
Ethylidyne		
Ru(0 0 1), Rh(1 1 1), Pd(1 1 1)		Rh(1 1 1)[LEED][k]
Ir(1 1 1), Pt(1 1 1)		Pt(1 1 1)[LEED][l]
C_2H_2 (low temperature)		
Type A	Perpendicular[m]	
Cu(1 1 1), Fe(1 1 1), Fe(1 1 0)		Cu(1 1 1)[PED][n]
Ni(1 1 1), Ni(1 0 0), Ru(0 0 1)		Ni(1 1 1)[PED][o], Ni(1 0 0)[STM][p]
Type A′		
Cu(1 0 0), Cu(1 1 0)		Cu(1 1 0)[STM][q], Cu(1 0 0)[STM][r]
Pd(1 0 0), Pt(1 0 0)		
Type B	'Di-σ/π' tilted[m]	
Ni(1 1 0), Pd(1 1 1), Pd(1 1 0)		Pd(1 1 1)[PED][s], Pd(1 1 1)[STM][t]
Ru(0 0 1), Ir(1 1 1), Pt(1 1 1)		Ni(1 1 0)[STM][u]

[a] The majority of the spectra are from VEELS and have been visually compared, reviewed and referenced in [46]; additional more recent results are reviewed in [47,48].

[b] Other spectra from Fe(1 1 1), Ru(0 0 1), and Pd(1 0 0), which show Type I features plus additional bands, are interpreted as either from a mixture of the two species or from an intermediate metallocyclopropane species [47].

[c] See the discussion in the text concerning the structural designations.

[d] This spectrum from Ni(1 0 0) shows an additional strong feature near 600 cm^{-1} which might be from an ethyne-like decomposition product of Type B [46,47].

[e] [49,66].

[f] At c(2 × 4) an asymmetrical short-bridge site on the ridge by PED [50]; located on the ridge by STM [51].

[g] An asymmetrical CH_2CH_2 structure across the hollow site [52].

[h] Another spectrum on Pd(1 0 0) shows a mixture of Type I and Type II species [46].

[i] On-top species on the ridge [53].

[j] The spectral, STM and PED all show unusual characteristics. The π-type spectra taken at 100 K show an unusual weakness or absence of the γCH_2 mode, implying substantial tilting relative to the surface [54]; the low-coverage STM suggests a short-bridged rather than an on-top structure [55]; and the higher-coverage PED is unable to distinguish between on-top or short bridge sites on the ridge [56]. More work is needed.

[k] [57].

[l] The LEED [58] study showed that the CC-bond was perpendicular to the surface and this led to the detailed spectroscopic assignment of the ethylidyne structure [46,47].

[m] Refers to the HCCH plane.

[n] [59,60].

[o] Same as footnote e.

[p] Long bridge across the diagonal [44,61] as anticipated spectroscopically using the impact selection rules [62,67]; also STM νCH data.

[q] Short bridge on the ridge [60].

[r] Long bridge, across the diagonal in the square unit mesh; also includes νCH data [44,61].

[s] [63].

[t] Hollow sites [64].

[u] Two species with CC symmetrically in the trough; consistent with the Type B spectroscopic result if the HCCH plane tilts towards a third metal atom in the ridge [51]: also STM νCH data.

consulted for the individual references. Additional VEEL references and more recent RAIRS studies of the same systems, which are particularly helpful in the better resolution and quality of their spectra in the νCH region, are given in more recent reviews [47,48]. The types of structures assigned to individual groups of spectra in terms of σ- or π-bonding contributions are given in inverted commas to denote an allowance for variations from the most symmetrical forms that can be envisaged for the chosen species. Many of the more recent PED or LEED studies have been carried out at coverages corresponding to particular high-coverage lattice arrays and, amongst the additional information that they provide, they sometimes reveal distortions such as CC-axis tilting or other displacements from ideal symmetries. Within the spectra such distortions can, and often do, give rise to weak additional absorptions that have become allowed. However, even in such cases, it is normally the bands allowed for the undistorted structure that continue to dominate the spectra in intensity terms.

Surface species derived from unsaturated hydrocarbons which are obtained at low temperatures are expected to involve non-dissociative adsorption in the sense that all interatomic linkages are retained in some form. In the case of ethene, the possibilities are limited to the opening up of the double bond to give di-σ adsorption to two, or less likely one, metal atom, or to π-bonding to the surface via a largely intact C=C. The first two possibilities form, in essence, dimetallic cyclobutane and monometallic cyclopropane species on the surface. Model compounds for all three possibilities exist in coordination chemistry [47]. In Table 1, the terms di-σ and π-bonded refer to the first and third possibilities which have been identified with Type I and Type II surface spectra. A few more complex low temperature spectra from ethene on Fe(1 1 1), Ru(0 0 1), and Pd(1 0 0) surfaces which, however, retain prominent Type I features, may be associated with mixtures of di-σ and π-bonded species or alternatively with metallocyclopropane structures.

The spectrum of the species formed at low temperatures from the adsorption of ethene frequently transform at higher temperatures into another readily recognisable pattern. This pattern mainly occurs on the (1 1 1) surfaces of f.c.c. metals or the (0 0 1) surface of h.c.p. metals and is now widely recognised to be from an ethylidyne species, CH_3–CM_3 (M = metal) [46,47]. This structure was definitively determined spectroscopically after an, in this case earlier, LEED study which indicated that the CC-bond of the species was perpendicular to the metal surface.

Three patterns of absorptions, labelled in table as Types A, A′ and B, were recognised amongst low temperature spectra from the adsorption of ethyne (see [48]). Based on considerations of the MSSR, together with group frequencies characteristic of species with hybridisation at the carbon atoms of between sp^2 and sp^3 (with particular attention to the presence or absence of an expected strong out-of-plane deformation mode of *cis*-disubstituted ethenes near 700 cm^{-1}), these species were attributed to complexes with the HCCH plane respectively perpendicular (A or A′) or at an intermediate tilted angle (B), with respect to the surface of the metal. In terms of bonding processes, the second of these is labelled, initially from spectroscopy, in Table 1 as di-σ/π, respectively. As the symbol implies, Type A′ spectra all retain the characteristics of Type A spectra with certain features showing additional intensity, often by impact excitation. As the relative intensities of dipolar and impact-excited features can depend on the acceptance angle of the spectrometer used, we assume that A′ spectra also imply perpendicular orientations of the HCCH plane.

The spectroscopic classifications are those given in the earlier reviews [46–48], where the relevant references are for the most part to be found. Recent additional spectroscopic data for ethyne on Ni(1 0 0) and Cu(1 0 0) have been remarkably obtained from individual adsorbed complexes by Ho and colleagues [44,45] using inelastic electron tunnelling spectroscopy (IETS) between the metal tip and the surface.

In the third column of Table 1 it is seen that, overall, the forms of the adsorbed species derived from the PED, LEED, or the more recent STM, methods are in excellent accordance with the earlier spectroscopic conclusions. Individual references are given for the diffraction and STM conclusions. The more direct methods provide, of course, additional site and quantitative bond-length and/or orientational information about the adsorbed complexes that is not derivable from spectroscopy.

5. Conclusions

The established vibrational spectroscopic method for deducing the structures of surface complexes involves the use of group-characteristic vibrations taking into account the requirements of the MSSR, followed by comparisons with the spectra of ligands in metal coordination or cluster compounds which are analogous to likely surface species. The results from applying this method to the spectra of C_2 adsorbed hydrocarbons are shown to have been extremely successful in anticipating the results of the more direct PED, LEED and STM methods. The spectroscopic methods additionally provide unique information on carbon hybridisation in the adsorbed species through the use of νCH data.

Less complete success has attended similar comparisons of spectroscopic and diffraction data for NO and CO. In the latter case, direct methods have shown that there is considerable, previously unanticipated, overlap of the spectroscopic regions attributable to adsorption on 2- and 3-fold (hollow) bridging sites for CO at substantial coverages. The reason for the lack of earlier spectroscopic recognition of this situation was a high coverage-sensitivity of the νCO modes coupled with the attribution of breaks in the νCO/coverage spectral sequences to different adsorption sites. The diffraction results showed that, in fact, these spectral breaks are related to different regular LEED-identifiable adsorption arrays involving the same 3-fold type of site. Although, as a result, there is overlap of the 2- and 3-fold spectral regions at higher coverages, nevertheless 2-fold/3-fold (and linear, on-top) distinctions remain unambiguous at low coverages. A minor overlap of the 2-fold/linear regions is readily distinguishable on coverage criteria so that ambiguities are also minimal near saturation coverages. The revised νCO ranges (cm^{-1}) for CO adsorption on various sites are as follows with the high wavenumbers corresponding to high coverages:

Linear (on-top) sites	2130–2000 cm^{-1}
2-fold bridged sites	2000–1870 cm^{-1}
3-fold (hollow) bridged sites	1950–1800 cm^{-1}

The high sensitivity of such spectra to coverage result from effects of vibrational couplings or static chemical interactions involving adjacent adsorbed molecules. The former only occurs when, as in the cases of νCO and νNO, the absorption bands are of quite exceptional strength. This consideration does not apply to the much weaker spectra of the C_2 species.

Improved characteristic spectroscopic regions are given for νNO for adsorption on different sites at low coverages as follows:

M–NO linear	1800–1720 cm^{-1}
M–NO bent	1700–1620 cm^{-1}
2-Fold sites	1570–1500 cm^{-1}
3-Fold sites	1470–1380 cm^{-1}

As in the CO case, higher coverages may be expected to cause overlaps between the different ranges.

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