PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1986 **318**, 141-161
doi: 10.1098/rsta.1986.0068

Phil. Trans. R. Soc. Lond. A **318**, 141–161 (1986)

Printed in Great Britain

Electron energy loss spectroscopy of adsorbed ethylene

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Electron energy loss spectroscopy (e.e.l.s.) provides an alternative method to infrared spectroscopy for studying the vibrational spectra of monolayers of chemisorbed molecules on single-crystal surfaces of metals. It has the advantages over infrared spectroscopy of considerably higher sensitivity, and the operation of two scattering mechanisms (dipolar and impact) that can be used to identify vibrations involving net motions parallel or perpendicular to the metal surface. It has the disadvantages with respect to infrared spectroscopy of lower attainable resolution and the necessity of the presence of only very low pressures (under 1 nbar) (0.1 mPa) from molecules in the gas phase over the surface.

Vibrational spectroscopy provides a powerful method for identifying the chemical structures of chemisorbed metal–adsorbate complexes. This is facilitated by an extensive existing vibrational spectroscopic literature. For work on metal surfaces, more recent infrared and Raman studies of ligands attached to metal clusters in compounds of known structure have also been of substantial assistance. The scope of this type of surface analysis will be illustrated by a review of the extensive and interesting results now available by e.e.l.s. from this and a number of other laboratories for the adsorption of ethylene on a variety of metals and crystal faces, and over a range of temperatures. At low temperatures, *ca.* 100 K, ethylene adsorbs on different crystal faces as a π-complex or a di-σ adsorbed complex. At room temperature, *ca.* 300 K, the low-temperature species are transformed in some cases into an ethylidyne complex, CH_3CM_3 (M = metal atom) or to a $(C_2H_2)M_4$ complex. More complex spectra, due to the presence of 4 different species, are obtained at room temperature by infrared transmission spectroscopy on finely divided oxide-supported metal catalysts. Three of these have been identified with the help of the e.e.l.s. results on metal single-crystal faces.

1. Introduction

In this paper we aim to show how electron spectroscopy, as a form of vibrational spectroscopy, can provide a powerful method of determining the structures of the new species formed by chemisorption on surfaces. The method at present is applicable in a particularly profitable manner to metal single-crystal surfaces. The species so identified can be very relevant to the understanding of the important subject of catalysis by metals and also to other surface processes such as corrosion and oxidation. The method in question is electron energy loss spectroscopy (e.e.l.s.), in which a mono-energetic electron beam is reflected off the surface in question, to give energy losses relating to quanta of energy that have been transferred to excite the vibrations of the adsorbed species (Ibach & Mills 1982).

Vibrational spectroscopy is a very powerful means of determining molecular structure. This is so (*a*) because vibrational spectra vary little from one phase to another – so that work done on related gaseous, liquid or solid samples (or on adsorbed species) can provide analogous information – and (*b*) because there is a very extensive literature available on the vibration frequencies of molecules, obtained over many years by experiments on pure substances by the more conventional methods of infrared or Raman spectroscopy (Bellamy 1975; Nakamoto 1978). By comparison with the study of pure substances, the problems of identifying the structures of chemisorbed species are more difficult because it is not possible to separate or isolate the surface complexes from the solid itself. However, the fact that vibrational spectra show many features that are characteristic of smaller chemical groups within larger molecular frameworks does mean that such spectra can provide reliable information about the general type of chemical identities of the surface complexes. In the context of organic molecules chemisorbed on metal surfaces, we shall show that the infrared and Raman spectra of metal cluster-compounds of known structures (the latter structures often determined directly by X-ray crystallography) can provide spectra from ligands attached to the metal atoms which closely correlate with the complete vibrational spectra of chemisorbed species (Howard *et al.* 1981; Skinner *et al.* 1981).

It might be asked why electron spectroscopy can advantageously be used for this purpose rather than, say, infrared reflection-absorption spectroscopy whereby an infrared beam is reflected from a metal surface and *en route* suffers absorptions from the adsorbed layers (Francis & Ellison 1959; Pritchard *et al.* 1975). The reason is that e.e.l.s. has major advantages in terms of sensitivity, normally by more than an order of magnitude, when it is used for spectral scanning over wide frequency or wavenumber ranges to obtain vibrational spectra from adsorbed monolayers and when comparison is made with infrared spectrometers that can likewise cover wide frequency ranges. An e.e.l. spectrometer can continuously scan a vibrational spectrum over nearly the complete range of fundamental vibration frequencies, from 4000 to *ca.* 100 $\mathrm{cm^{-1}}$. For this type of frequency coverage, in the infrared region only the less-sensitive thermal detectors can be used, such as thermocouples or pyroelectric detectors. Even after the full advantages of modern infrared interferometry coupled with Fourier-transform analysis have been taken into account, there remains a disadvantageous sensitivity gap in comparison with e.e.l.s. The infrared situation is more advantageous when a narrow frequency range is required, which can be matched with a high-sensitivity photoconductive detector, or when the bands are particularly sharp so that the resolution advantage of the infrared method can be utilised. For wide frequency ranges the high-sensitivity liquid-helium cooled bolometer also holds out the promise of improved infrared performance in the future.

Although there are some complementary disadvantages of e.e.l.s. compared with the photon spectroscopies, such as limited resolution and the acceptability of only limited gas pressures over the surface (Chesters & Sheppard 1981), there is no question that the high sensitivity of e.e.l.s. has opened up the field of vibrational spectra of adsorbed species in a very advantageous way. Acceptable spectra can now be obtained from fractions of a monolayer of almost all adsorbates on metal surfaces. Further developments will improve accessibility to similar information from adsorption on non-metal surfaces although – unlike with metal surfaces – in such cases the spectrum is more likely to be dominated over certain energy regions by an electron loss spectrum from the solid adsorbent itself (Cox *et al.* 1982, 1983).

2. INTENSITIES, SELECTION RULES AND SYMMETRIES OF ADSORBED MONOLAYERS

It is clear that there are at least two general mechanisms involved in the transfer of vibrational quanta to an adsorbed monolayer. A third, resonance, mechanism can be involved for specific energies of the incident electron beam (Ibach & Mills 1982).

2.1. *The dipolar mechanism*

This mechanism is a long-range one whereby the changing electrical field at the surface that is caused by the incoming electron excites surface vibrations through the oscillatory electrical dipole moment associated with a vibrationally excited molecule (Ibach 1977). Because on metal surfaces all the electrical lines of force near the surface are perpendicular to it, this mechanism excites those modes that have vibrational dipole moments perpendicular to the surface (Francis & Ellison 1959; Pearce & Sheppard 1976). In general, these are the vibrations that preserve the full symmetry of the adsorbate–adsorbent complex (Sheppard & Erkelens 1984). This restrictive behaviour is sometimes termed the metal-surface selection rule. Vibrations for which the associated dipole changes are strictly parallel to the surface are forbidden under the dipolar mechanism and this distinction can provide a useful criterion for vibrational assignment. In experimental terms, it is very advantageous that the dipolar mechanism also gives rise to reflected electrons that are closely channelled in the specular direction, i.e. where the angle of reflection equals the angle of incidence (Ibach 1977).

The same selection rule, and the same dependence of the intensity on vibrational dipole changes, characterizes infrared reflection–absorption spectra. Although in comparison with infrared spectra the relative intensities within an e.e.l. spectrum tend, for experimental reasons, to fall off with increasing vibration frequency (increasing energy loss), it is very advantageous, as we shall show, that the strong features in e.e.l. spectra taken in the specular direction are normally associated with strong infrared bands of modes that have dipoles perpendicular to the metal surface. The quantitative frequency and qualitative intensity relations between infrared spectra and e.e.l. spectra associated with dipolar excitation will be shown to be very valuable.

2.2. *The impact mechanism*

This is a short-range vibrational excitation mechanism, analogous to that associated with low-energy electron diffraction except that the reflection process is an inelastic one (Ho *et al.* 1978). This type of reflection scattering process is relatively diffuse, i.e. electrons are scattered over a wide range of angles, and the signal is hence relatively weak in a particular direction. Electrons scattered by this mechanism are best observed separately from those scattered by the dipolar mechanism by making measurements 5° or more 'off-specular', where the dipolar contribution has fallen to a small value.

Several selection rules associated with the impact mechanism have also been evaluated (Tong *et al.* 1980, 1981; Li *et al.* 1980; Aers *et al.* 1981), and may be summarized as:

(i) If the vibration to be excited is antisymmetric to a 2-fold symmetry axis perpendicular to the metal surface there will be no impact scattering in the specular direction although intensity will be observed off-specular.

(ii) If the vibration is antisymmetric with respect to a plane of symmetry perpendicular to the metal surface and to the plane of incidence again there will be no impact scattering in the specular direction, but such scattering will be observed off-specular in the plane of incidence.

(iii) If the vibration is antisymmetric with respect to a plane of symmetry perpendicular to the metal surface and parallel with the plane of incidence, there will be no impact scattering in any direction within that plane, although impact scattering may be observed in the plane at right-angles.

Under these selection rules, once again the completely symmetrical vibrations will be active in the specular direction, although they usually give rise to weaker features than the dipolar-excited modes, for which the reflected electrons are concentrated in that direction. All vibrations associated with net motions strictly parallel to the surface fall into one or other of the categories (i)–(iii). In the first two cases, they can give rise to off-specular electrons in the plane of incidence; in the third case, they only give rise to off-specular electrons outside the plane of incidence.

This capability of detecting parallel as well as perpendicular vibrations is an important property of e.e.l.s., which is not shared by infrared spectroscopy (Ibach & Mills 1982). It was originally demonstrated for hydrogen adsorbed on W(100) faces, where the hydrogen atoms bridge pairs of metal atoms (Ho *et al.* 1978).

It has been mentioned above that qualitative relative intensity analogies can be expected between infrared spectra and on-specular e.e.l. spectra of adsorbed species, because the latter are normally also expected to be dominated by the dipolar scattering mechanism. A persistent discrepancy occurs in our on-specular spectra of adsorbed hydrocarbons on metals where the high-frequency CH bond-stretching modes near 3000 cm^{-1} are seen mostly to be excited by the impact mechanism. Whereas dipolar contributions in infrared spectra are normally comparatively large, the intensities of these losses in the e.e.l. spectra change little on changing to a considerable off-specular angle. However, although the best mean direction for observing dipolar-scattered electrons is close to the specular one, increasing magnitudes of energy losses imply that the peak direction of scattered electrons are rather closer to the surface normal than the specular direction (Newns 1980). The angle of deviation from specular increases with the ratio of the energy loss to the energy of the incident electron beam. For a relatively narrow angular aperture of the electron-energy analyser, and lower energies of the incident electron beam, a considerable proportion of the dipolar scattered electrons for high-energy losses will fall outside the solid angle collected by the analyser. When this is the case, a higher proportion of impact-scattered electrons are picked up on-specular. This type of effect can cause increasing differences between the relative intensities of infrared and specular e.e.l. spectra for the higher energy (frequency) losses. Hence e.e.l.s. spectrometers with higher collection apertures, or which use higher impact energies, tend to give higher intensities from increasing dipolar contributions in the high-energy loss region.

2.3 *The symmetry properties of adsorbed layers*

This subject has been given systematic discussion elsewhere (Sheppard & Erkelens 1984). A starting point is the set of symmetry properties of the bare surface. It can be shown that the only possible symmetry elements are reflection planes or axes of symmetry perpendicular to the surface, and that these should be evaluated by taking the three-dimensional lattice of the adsorbent into account, and not just the top two-dimensional layer. An isolated adsorbate–adsorbent complex, such as can be expected to occur at low surface coverage, will retain certain of the symmetry elements associated with the bare surface, but will often destroy others. It is the residual symmetry elements that have to be taken into account in making use of the selection rules described above.

As the coverage of the surface by adsorbate species builds up, some of the symmetry elements associated with an isolated adsorption complex may be destroyed, for example by the occurrence of near-neighbour adsorbates in certain directions but not in others. The analogy here is with the vibrational spectra of molecules in liquids where, strictly speaking, no selection rules apply.

At higher coverages regular arrays of adsorbed molecules will be formed. When these are sufficiently extensive, all but the adsorption complexes near edges or defects in the array will now have effective symmetry appropriate to the site that it would occupy in an infinite regular array. The surrounding molecules now play a role in determining the symmetry of an individual complex, and in such cases a systematic set of symmetry elements associated with an isolated surface complex will often be lost. The two-dimensional regular array will have repeated primitive unit cells (unit meshes), which often contain more than one adsorbed species. The point is illustrated in figure 1 for the unit mesh of a $c(4\times2)$ regular overlayer from CO molecules adsorbed in Ni(111). Here more than one bridged CO species (CO molecules that are adsorbed perpendicular to the surface bonded to two metal atoms) exists in the primitive unit mesh. Within such a set of symmetry-related adsorption complexes within the unit cell, vibrations of the pairs of complexes may vibrate in-phase or out of phase. This is illustrated in figure 2, where + and − denote in-phase or out-of-phase relations between otherwise identical normal modes of vibration of the two molecules in the unit cell (Sheppard & Erkelens 1984).

Most analyses of e.e.l. spectra to date have been made in terms of the symmetry properties

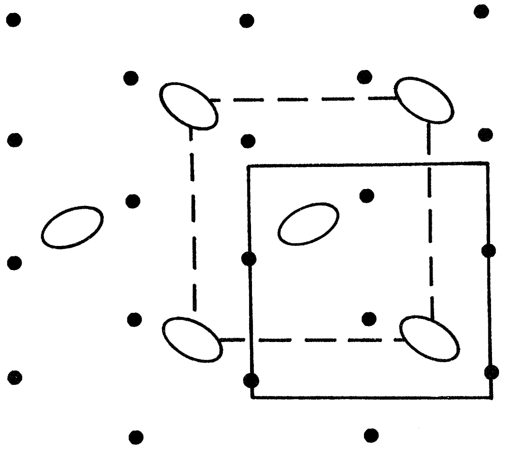

FIGURE 1. The $c(4\times2)$ regular array of CO molecules on a Ni(111) surface. Two alternative two-dimensional primitive unit cells (unit meshes) are outlined. The black circles represent metal atoms and ellipses indicate twofold bridged CO molecules. (Diagram adapted from Sheppard & Erkelens 1984.)

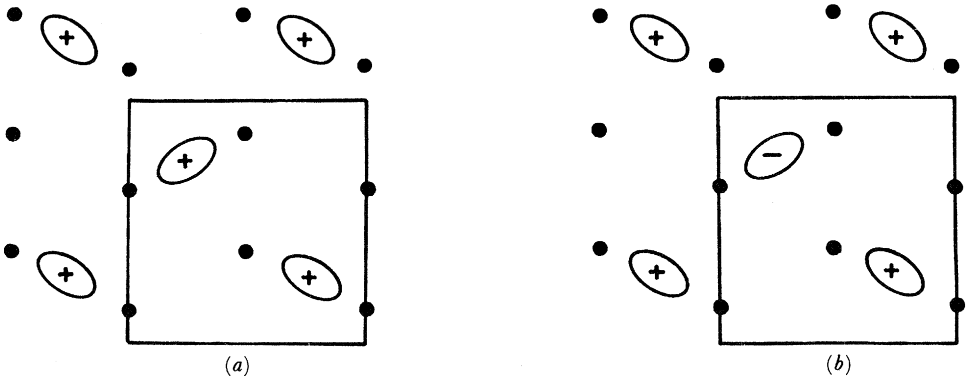

FIGURE 2. A schematic representation of (a) the in-phase and (b) out-of-phase relations of vibrations of the two symmetry-related CO adsorbate molecules within the two-dimensional unit cell (+, in-phase; −, out of phase; diagram adapted from Sheppard & Erkelens 1984).

of an isolated complex. Quite often the stronger features of the spectra have been successfully interpreted on-specular as arising from a rather symmetrical surface complex, but the occurrence and behaviour of weaker specular on non-specular features have led to conclusions that additional distortions are present. If irregular adsorption occurs at non-fractional coverages, these extra features (which, of course, are real in their implications) may be associated with non-symmetrical surroundings of what would otherwise be a symmetrical complex. The presence of *regular* arrays of adsorbed species is best detected (and characterized) by low-energy electron diffraction (l.e.e.d.). It is hence particularly important that, where possible, e.e.l. spectra measurements are made in conjunction with l.e.e.d. studies under conditions where the regular diffraction spots are best defined. Only under these circumstances can the symmetry-based selection rules associated with e.e.l.s. be strictly applied and the symmetries of arrays of surface complexes be properly evaluated. It would seem to be worthwhile to make more comparative e.e.l.s. studies in the presence and absence of good l.e.e.d. patterns with this consideration in mind. In the meantime, some caution is needed in interpreting weak features of spectra as providing evidence for unsymmetrical adsorption sites, unless the l.e.e.d. diffraction pattern is well defined.

To give an analogy from an earlier era of vibrational spectroscopy, the infrared and Raman spectra of liquid benzene showed a sufficiently large number of weak features, including features in common between the two types of spectra, that the question was raised whether the benzene molecule had really the shape of a regular hexagon, which was strongly expected on theoretical grounds. With careful gas-phase measurements, and by analysis of the spectra of a wide range of $C_6H_{6-n}D_n$ species (an analysis that led to a sequence of 21 publications, beginning with Ingold *et al.* 1936 and ending with Ingold *et al.* 1946), it was finally concluded that benzene did indeed have the symmetrical structure suggested by valence theory! Many of the weak features were shown to have arisen from the effects of relatively weak inter-molecular forces on the benzene molecules in the liquid or crystalline phases. Although non-polar, benzene molecules have moderately high electrical polarizability because of the presence of their π-electrons.

3. EXPERIMENTAL

The studies described in this paper were made in an ultra-high vacuum system (Leybold-Heraeus ELS22) (5×10^{-11} mbar† base pressure) equipped for electron energy loss spectroscopy (e.e.l.s.), low-energy electron diffraction (l.e.e.d.), Auger electron spectroscopy (a.e.s.) and quadrupole mass spectroscopy. E.e.l. spectra were recorded by using a primary beam energy of 3 eV incident with the sample at an angle of 60° with respect to the surface normal. This angle of incidence was maintained in spectra recorded both in the specular and off-specular directions. The scattering plane was approximately parallel to the ⟨110⟩ direction on the (110) faces of the face centred cubic (f.c.c.) metals Ni and Pd.

In the experiments discussed in the following section a resolution of 4–5 meV (32–40 cm^{-1}) and greater than 10^5 events s^{-1} was routinely achieved in the elastically scattered beam from the clean sample. The resolution employed in recording the spectra of the adsorbed ethylene was more commonly 5–8 meV (40–64 cm^{-1}) depending on the desired signal to noise characteristics.

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† 1 bar = 10^5 Pa.

The metal sample was prepared by mechanical polishing followed by cycles of argon-ion bombardment and annealing in vacuo. Surface cleanliness was monitored by a.e.s., l.e.e.d. and e.e.l. spectroscopy. Ethylene acetylene gas, research grade (B.O.C.) and ethylene-d_4, 99.99% atom D (Merck, Sharp and Dohme) were used without further purification.

The finely divided Pt and Pd catalysts were prepared by the impregnation method. High-area non-porous silica, Cabosil H5, of area 250 to 300 $m^2\ g^{-1}$ was co-deposited with an appropriate water-soluble metal compound (hexachloroplatinic acid for Pt and palladium chloride for Pd). The resulting powder was pressed into a 1″ diameter (2.54 cm) disc of mass *ca.* 50 mg and transferred into the evacuable infrared cell. The metal compound was reduced to the metal with hydrogen at 400 °C. After evacuation overnight at the latter temperature, the disc was cooled to room temperature before adsorption of ethylene. Infrared spectra were measured with a Digilab FTS-14 Fourier-transform spectrometer at a resolution of 2 cm^{-1}; the metal–silica background spectrum was subtracted to give the spectrum above 1300 cm^{-1} from the adsorbed species. Below 1300 cm^{-1} the silica disc absorbs all the infrared radiation.

4. The application of e.e.l.s. to the study of ethylene (ethene) adsorbed on single-crystal metal surfaces

We have chosen the adsorption of ethylene on metal surfaces as an example to illustrate how the structures of adsorbed species can be well characterized by e.e.l.s. In our own laboratory we have studied by this means the adsorption of ethylene on the (110) faces of nickel and palladium (Anson *et al.* 1983 *a*, *b*; Chesters *et al.* 1985). Other laboratories have similarly studied ethylene adsorption on (111) faces of platinum (Ibach & Lehwald 1978; Steininger *et al.* 1982); palladium (Gates & Kesmodel 1982 *a*); nickel (Lehwald & Ibach 1979); and the (100) face of copper (Nyberg *et al.* 1982). We wish to show first of all that several distinct general patterns of spectra can be discerned in the collection of spectra, and that rather convincing general structural assignments can be made from most of these spectral patterns. To make optimum use of similarities between infrared and e.e.l. spectral intensities, we shall pay particular attention to the e.e.l.s. results obtained in the specular direction. However, much useful additional information can be derived from off-specular spectra. Where particularly informative, the latter results will also be described.

Figure 3 shows spectra obtained in our laboratory for ethylene and perdeuteroethylene adsorbed at low temperatures on Ni(110) with a clean metal surface (Anson *et al.* 1983 *a*), on Ni(110) with a carbided surface (Anson *et al.* 1983 *a*) obtained by heating the metal crystal in the presence of ethylene at 573 K, and on a clean Pd(110) surface (Chesters *et al.* 1985).

It can be seen at once that the spectra derived from C_2H_4 on the clean Ni(110) and Pd(110) surfaces are very different. We shall summarize below the evidence that these different spectra arise from the two probable types of $C_2H_4(C_2D_4)$ species that have been widely discussed in the chemisorption and catalyst literature, namely a di-σ-adsorbed species of local formula MCH_2CH_2M (M = metal atom) and a π-adsorbed species of formula $(C_2H_4)M$. It can also be seen in figure 3 that the spectrum from ethylene on the carbided Ni(110) surface is notably different from that on the clean surface and – despite a number of differences in relative intensities of some of the bands – that there is resemblance between the spectrum on carbided nickel and that on clean Pd(110), particularly in frequency terms. We have previously concluded (Anson *et al.* 1983*a*, *b*) that the spectral change from the clean to the carbided Ni(110) surface denotes a change from a di-σ-adsorbed to a π-adsorbed species.

All three spectra in figure 3 were taken at low temperatures, as is indicated in the figure caption. It is under such conditions that the adsorbed species are most likely to retain the original hydrocarbon grouping of CH_2CH_2, implying that no breaking of any of the CC or CH bonds has occurred. However, for the di-σ-adsorbed species there has been a reduction in the CC bond order from two to nearly one.

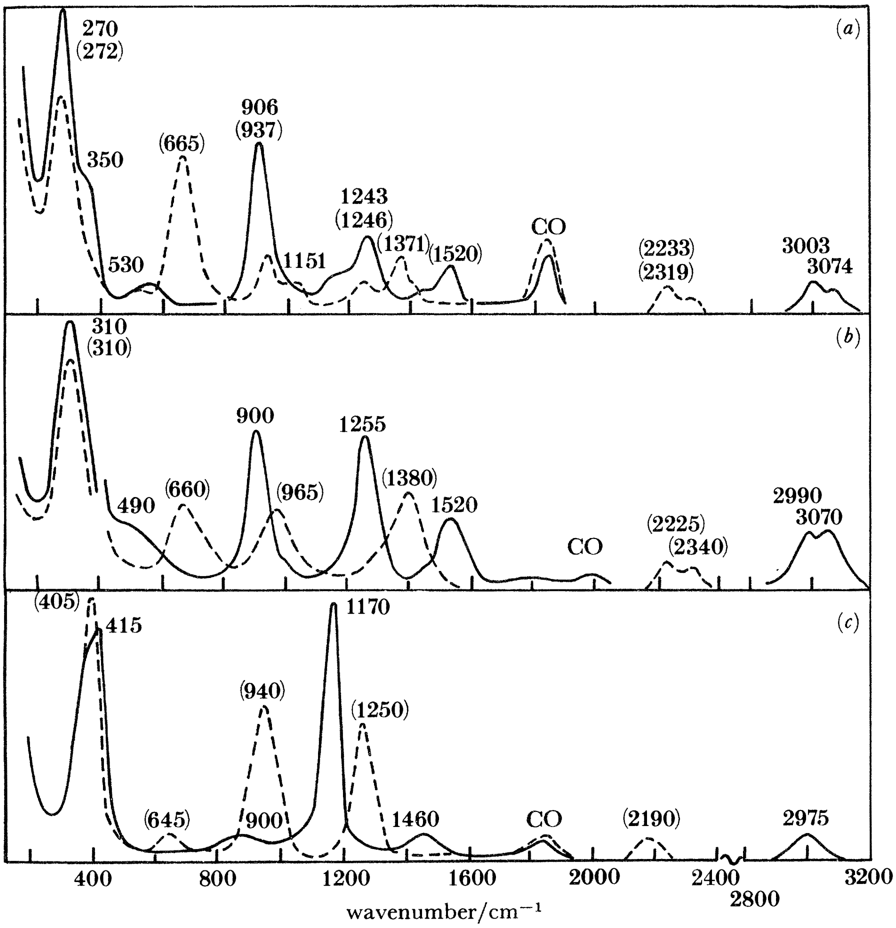


FIGURE 3. The electron energy loss spectra of ethylene, C_2H_4, and perdeuteroethylene, C_2D_4, adsorbed (*a*) on clean Pd(110); (*b*) on carbided Ni(110); and (*c*) on clean Ni(110) surfaces at 110 K. The wavenumber values for adsorbed C_2D_4 are shown in brackets. Solid lines, C_2H_4; broken lines, C_2D_4.

Considerable changes in the spectra derived from chemisorbed ethylene occur on raising the temperature from *ca.* 100 K to *ca.* 300 K. This is illustrated in figure 4, which shows spectra from ethylene on Pd(110) and Pt(111) at 300 K. The *ca.* 300 K spectra on the Pt(111) surface are illustrated from the work of Ibach and his colleagues (Ibach & Lehwald 1978; Steininger *et al.* 1982); those on Pd(110) are results from our own laboratory (McDougall 1985). Both spectra from ethylene at 300 K are notably different from the low-temperature spectra (see figure 3 for Pd(110) and Ibach & Lehwald (1978) for Pt(111)). The two spectra from ethylene adsorbed at 300 K are also very different from each other. But it is of interest that in each case

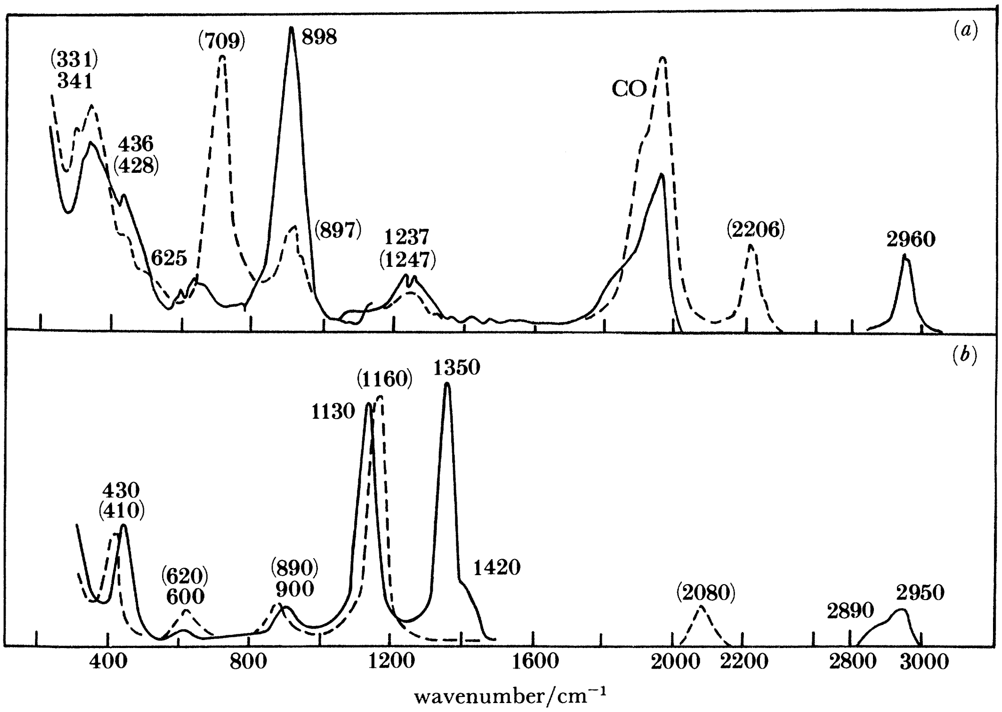


FIGURE 4. A comparison of the electron energy loss spectra of C_2H_4 adsorbed on (*a*) the Pd(110) face at *ca.* 300 K and (*b*) the Pt(111) face at over 340 K. The Pt(111) spectra are reproduced by permission from Steininger *et al.* (1982). The wavenumber values for adsorbed C_2D_4 are shown in brackets. Solid lines, C_2H_4; broken lines, C_2D_4.

they are very similar to those from acetylene on the same metal surface at the same temperature (Ibach & Lehwald 1978; McDougall 1985).

The 300 K spectrum on Pt(111) has in the past been the subject of much work and interpretive speculation because of the importance of such metals for the hydrogenation of alkenes to alkanes near room temperature. We were able to show that the surface species in question is CH_3CPt_3, by comparing the spectrum from ethylene at 300 K with the infrared spectrum from an inorganic metal-cluster compound of known structure, $(CH_3C)Co_3(CO)_9$ (Skinner *et al.* 1981), bearing in mind the operation of the metal-surface selection rule (§2). In this surface species the central carbon atom is equally bonded to three Pt atoms at the corner of an equilateral triangle. For the model compound, the a-modes correspond to those of the surface complex that would give vibrational dipole moments perpendicular to the surface: the e-modes of the model compound correspond to those with dipoles parallel to the surface and were picked up as additional features in the e.e.l. spectra taken in off-specular directions (Baró & Ibach 1982, unpublished work, illustrated in Ibach & Mills 1982). The degree of agreement between the spectra of the surface complex and the model cluster compound is shown in table 1. The empirical composition of this surface complex is C_2H_3, i.e. it is richer in hydrogen than is acetylene. In fact the spectrum in question for acetylene was taken in the presence of co-adsorbed hydrogen (Ibach & Lehwald 1978). It is clear that by 300 K, near room temperature, CH bonds of the original adsorbed ethylene molecule have been broken before rearrangement leading to the remaining hydrogen atoms being finally attached to only one of the two carbon atoms.

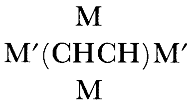
TABLE 1. A COMPARISON OF THE INFRARED SPECTRUM OF THE MODEL COMPOUND $(CH_3C)Co_3(CO)_9$ AND THE ON-SPECULAR AND OFF-SPECULAR ELECTRON ENERGY LOSS SPECTRA FROM ETHYLENE ADSORBED ON Pt(111) AT *ca.* 300 K

(Notation: (s) strong; (m) medium; (mw) medium weak; (w) weak; ν, bond-stretching; δ, angle-bending; s, specular; os, off-specular. The notations a_1 and e denote vibrational symmetry classes; relative to the plane of the M_3 triangle (M = metal), a_1 denotes a perpendicular mode and e, a parallel mode. These should, and do, correspond to specular (dipolar) and off-specular (impact) excited modes of the surface species.)

e.e.l. spectrum[2] of C_2H_4 on Pt(111)/cm^{-1}	assignment	infrared spectrum[1] of $(CH_3C)Co_3(CO)_9/cm^{-1}$
2940 (w) os	νCH_3 (as)	2930 (m) e
2910 (m) s	νCH_3 (s)	2888 (m) a_1
1420 (w) os	δCH_3 (as)	1420 (m) e
1355 (s) s	δCH_3 (s)	1356 (m) a_1
1130 (s) s	νC–C	1163 (m) a_1
1000 (w) os	CH_3 rock	1004 (s) e
900 (mw) s	[νMHM]	—
435 (m) s	νCM_3 (s)	401 (m) a_1

[1] Howard *et al.* (1981).
[2] Baró & Ibach (1982).

For ethylene on the Pd(110) surface at 300 K, the spectrum differs from that of ethylene on Pd(110) at 100 K (figure 3), which we have previously assigned to the C_2H_4–metal π-complex (Chesters *et al.* 1985), by two notable features. First, the e.e.l. band in the 3000 cm^{-1} region has changed from a pair of overlapping bands near 2980 and 3050 cm^{-1} to a single sharp one at *ca.* 2960 cm^{-1}. These bands arise from CH bond-stretching vibrations and the frequency denotes a change from the expected sp^2 hybridized carbon atoms for the low-temperature species to ones more closely similar to sp^3 at 300 K. Secondly, there is no trace in the spectrum of the *ca.* 1520 cm^{-1} band of the low-temperature ethylene spectrum, which is characteristic for the coupled ν$C{=}C$ vibration of π-complexes (see figure 3). The overall simplicity of this spectrum suggests that there are few CH bonds present, probably one or two. A very reasonable assignment would be to a symmetrical $(CHCH)M_4$ surface complex, which is di-σ-bonded to two metal atoms in the trough of the (110) surface with di-π-bonding to metal atoms on the exposed rows. This has the geometry



$$\begin{array}{c} M \\ M'(CHCH)M' \\ M \end{array}$$

where M denotes a metal atom in the upper rows of metal atoms on the (110) surface and M′ denotes a metal atom at the bottom of the trough.

A reasonable vibrational assignment for this structure would be 2960 (νCH), 1237 (νCC), 900 (δCH sym.), 625 (γCH sym.) and 436 cm^{-1} (νCM), where ν, δ and γ denote, respectively, bond-stretching, and in-plane deformation and an out-of-plane deformation modes. Some of the extra absorption near 340 cm^{-1} is caused by the co-existence of CO on the Pd(110) surface. On the assumption of C_{2v} symmetry for the complex, all the e.e.l. spectral features can be assigned to completely symmetrical vibrations in accordance with the metal surface selection rule, with the exception of the weakest one at 625 cm^{-1}. The analogous spectrum from adsorbed C_2D_2 shows the strong band near 680 cm^{-1} with an isotopic ratio of 1.32 relative to the corresponding band in the C_2H_2 spectrum. This is in reasonable expectation for δCH/δCD.

It is seen that by 300 K for Pd(110), as well as for Pt(111), some of the original CH bonds of the adsorbed ethylene have been broken. The spectrum from acetylene on Pd(110) at 300 K differs substantially from that at 110 K (McDougall 1985; Bandy *et al.* 1984). The latter, again by analogy with the spectra of an appropriate metal cluster compound, has been assigned to a di-σ/π-complex involving only three metal atoms (Anson *et al.* 1983*b*).

Three of the four different types of spectra discussed above have been obtained several times on other metals or other surfaces of the same metal. Illustrative sets of on-specular spectra, taken from the wider literature, are summarized schematically for adsorbed C_2H_4 and adsorbed C_2D_4 in figures 5–7. The positions, relative heights and half-widths of the schematic triangular bands relate to the values in the original published spectra. The references are indicated in the figure captions. Also illustrated at the top of each of these figures are the positions of the relevant

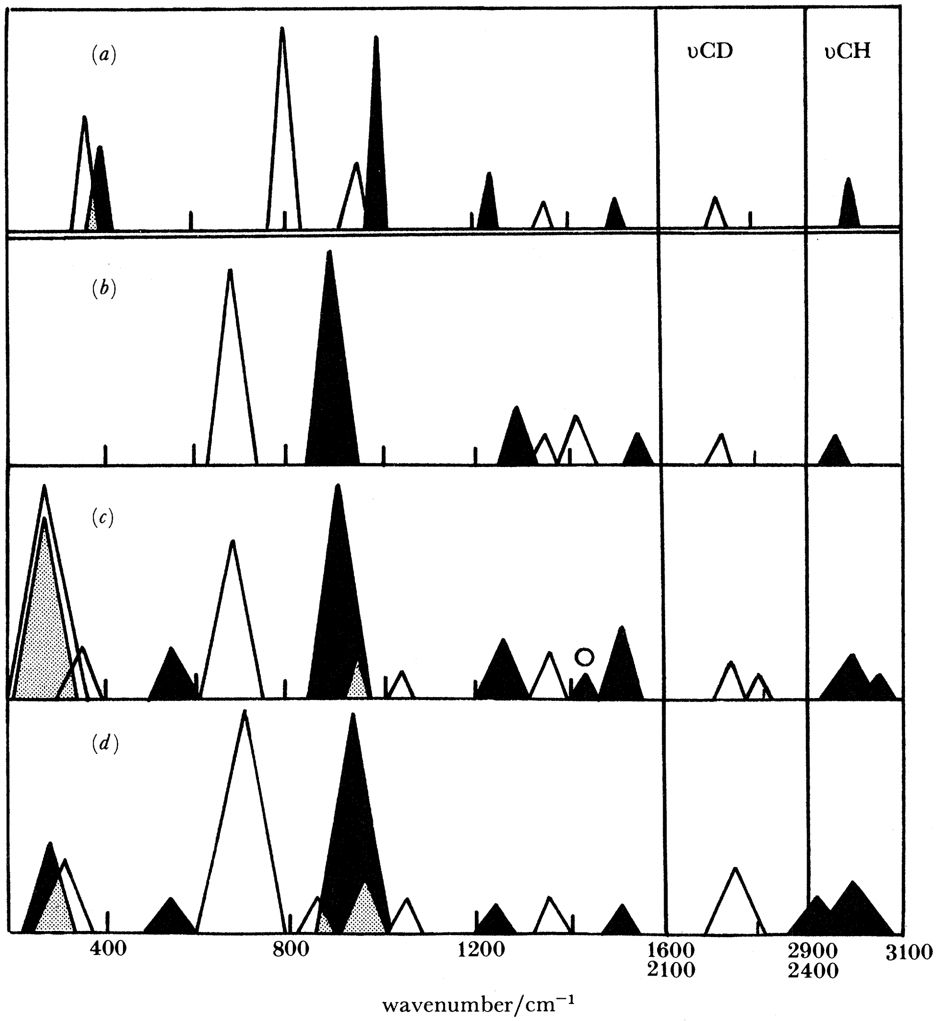


FIGURE 5. Schematic comparisons of the vibrational spectra from $(C_2H_4)M/(C_2D_4)M$ π-complexes (M = metal atom). (*a*) The infrared spectra from K^+ $[(C_2H_4)PtCl_3]^-H_2O$ as a model compound. Only the bands from completely symmetrical modes (corresponding to those allowed on metal surfaces by the dipolar selection rule) are shown. (*b*) e.e.l. spectrum on Cu(100) at 80 K (Nyberg *et al.* 1982). (*c*) e.e.l. spectrum on Pd(110) at 110 K (figure 3). (*d*) e.e.l. spectrum on Pd(111) at 150 K (Gates & Kesmodel 1982*a*). Bands from the presence of small amounts of the di-σ-adsorbed species have been omitted (Chesters *et al.* 1985). Bands from C_2H_4 are in solid black, those from C_2D_4 are outlined in black and overlapping bands are shaded.

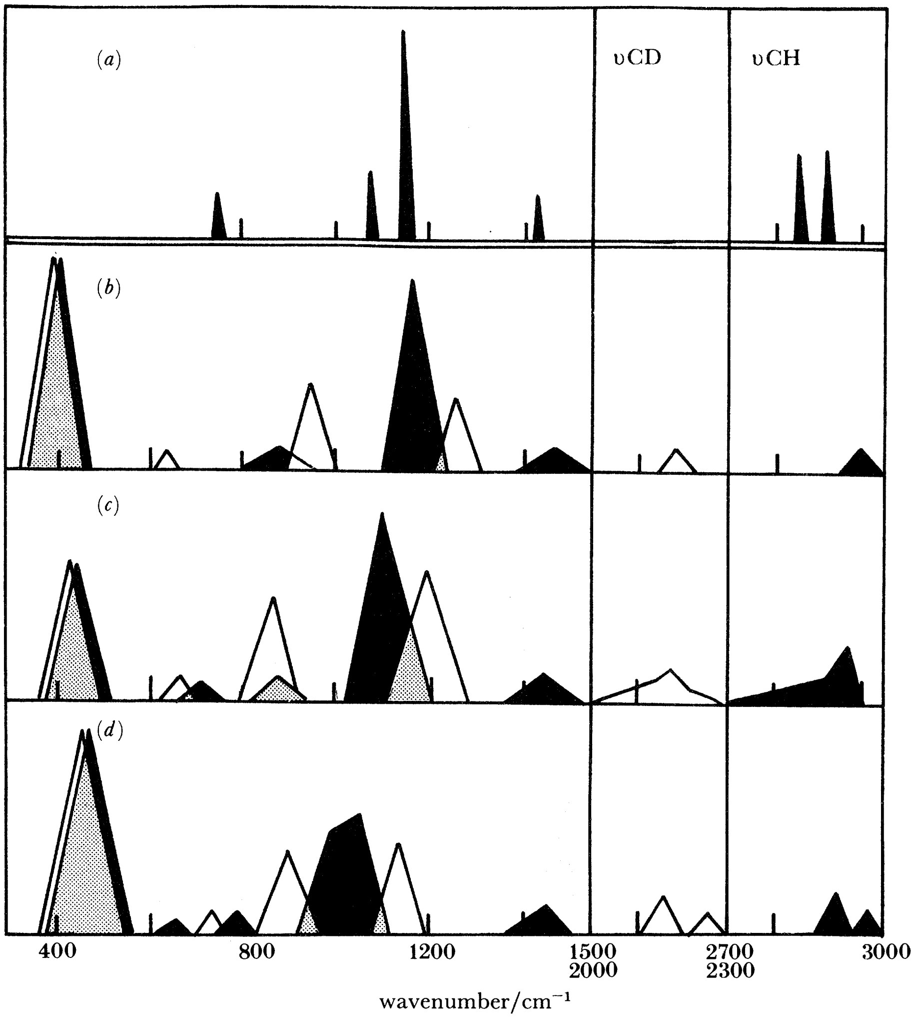


FIGURE 6. Schematic comparisons of the vibrational spectra from di-σ-adsorbed complexes, MCH_2CH_2M and MCD_2CD_2M (M = metal atom). (*a*) Spectrum from $(C_2H_4)Os_2(CO)_8$ as model compound, a provisional assignment of the completely symmetrical modes (C. E. Anson, unpublished work). (*b*) e.e.l. spectrum on Ni(110) at 110 K (figure 3). (*c*) e.e.l. spectrum on Ni(111) at 110 K (Lehwald & Ibach 1979). (*d*) e.e.l. spectrum on Pt(111) at 220 K (Steininger *et al.* 1982). Bands from C_2H_4 are in solid black, those from C_2D_4 are outlined in black and overlapping bands are shaded.

infrared bands in the spectra of metal cluster compounds of indicated known structures. The relevant bands are those of the completely symmetrical vibrations of the surface complex, which would give perpendicular dipole changes on a metal surface. It is seen that, although the detailed positions of the bands from the model compounds differ to a degree from those of the analogous features in the e.e.l. spectra (there are also frequency differences between the spectra of the different adsorbed species), the family resemblances between the spectra are very clear when the positions and relative intensities of the bands are taken into account. For the spectra assigned to the $(C_2H_4)M$ π-complex and to the CH_3CM_3 (ethylidyne) species (figures 5 and 7), the identification of the completely symmetrical vibrations of the hydrocarbon ligands is taken from detailed and complete analyses of the vibrational spectra of the model compounds (Hiraishi 1969; Grogan & Nakamoto 1966; Skinner *et al.* 1981). For the MCH_2CH_2M species,

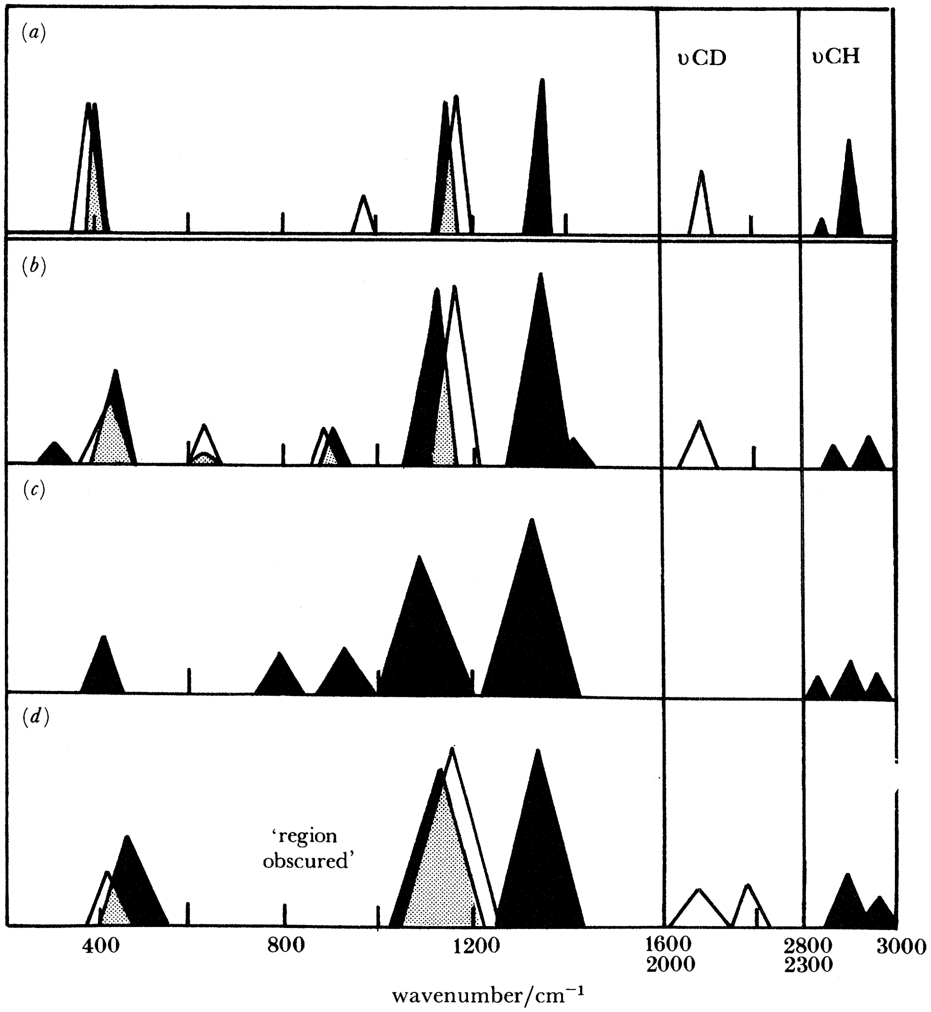


FIGURE 7. Schematic comparisons of the vibrational spectra from the ethylidyne species, CH_3CM_3 and CD_3CM_3 (M = metal atom). (*a*) Infrared spectrum, completely symmetrical modes, of $(CH_3C)Co_3(CO)_9$ (Howard *et al.* 1981) and $(CD_3C)Co_3(CO)_9$. (*b*) e.e.l. spectrum on Pt(111) at over 340 K (Steininger *et al.* 1982). (*c*) e.e.l. spectrum on Pd(111) at 300 K (Kesmodel & Gates 1982*a*). (*d*) e.e.l. spectrum on Rh(111) at over 270 K (Dubois *et al.* 1980). Bands from C_2H_4 are in solid black, those from C_2D_4 are outlined in black and overlapping bands are shaded.

the choice of the completely symmetrical modes seems to be a reasonable one from a recent study of the infrared spectrum of $(C_2H_4)Os_2(CO)_8$ by C. E. Anson (1985, unpublished work), but has not yet been supported by analogous spectra from the C_2D_4 compound.

5. A COMPARISON WITH INFRARED SPECTRA FROM ETHYLENE ADSORBED ON SILICA-SUPPORTED PLATINUM AND PALLADIUM

The identification of the structures of specific adsorbed species from ethylene on metal surfaces is of significance in relation to the mechanisms of catalytic reactions involving the adsorbate and the appropriate metal (for example the catalytic hydrogenation of alkenes to alkanes). It is therefore of very considerable interest to see what vibrational spectra can be obtained from ethylene adsorbed on finely divided silica-supported metals. Such spectra cannot be obtained by e.e.l.s., but have been obtained in this laboratory by infrared transmission spectroscopy at room temperature (Morrow & Sheppard 1969; Prentice 1977; Pearce 1974; Lesiunas 1975; Prentice *et al.* 1976; James 1984; McDougall 1985).

The use of the high sensitivity of Fourier-transformation infrared interferometry, allied with the ratioing facility provided by the incorporation of a minicomputer in the spectrometer, does enable good quality transmission spectra to be obtained down to a cut-off wavenumber determined by the lattice absorptions of the oxide support. The use of silica as a support results in accessible spectra from the ethylene adsorbate down to 1300 cm^{-1}.

Typical infrared spectra for ethylene adsorbed at room temperature on silica-supported Pt and Pd samples are shown in figure 8 (Morrow & Sheppard 1969; Prentice *et al.* 1976; James 1984). Also given in the figure captions are the probable structural assignments of the main bands, taking into account the results from the more recent e.e.l.s. studies. At earlier stages the π-complex had been identified in these spectra as giving absorptions at 3015 and at 1500 cm^{-1} on Pt and 2985 and 1510 cm^{-1} on Pd (Prentice *et al.* 1976). The fact that these bands occur at room temperature in the spectra from the finely divided metal catalysts, whereas those from the π-complex spectra shown in figure 5 are all obtained at lower temperature,

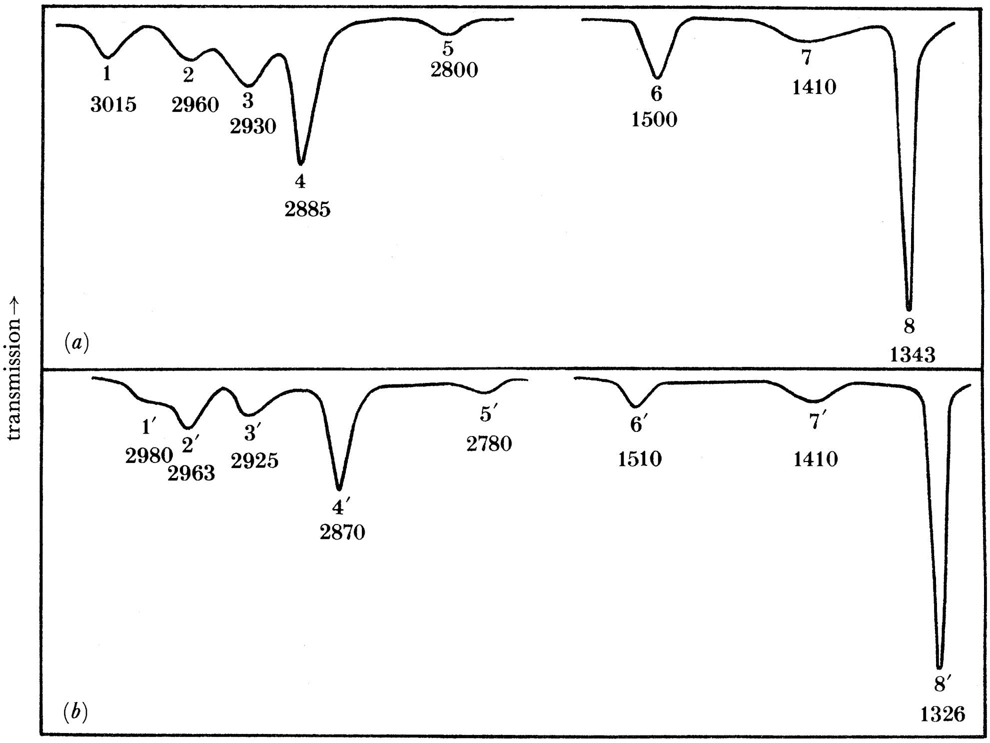


FIGURE 8. Infrared spectra of ethylene adsorbed at room temperature on finely divided metal catalysts (*a*) Pt–SiO_2 and (*b*) Pd–SiO_2 at *ca.* 300 K (James 1984; McDougall 1985). The assignments of the absorptions to the presence of particular species are given below and have been made in comparison with the spectra of model compounds and with ethylene spectra on metal single-crystals, as schematically illustrated in figure 5–7. The spectrum of the catalyst background has been removed by ratio analysis, but a silica blackout precludes the observation of bands at under 1300 cm^{-1}. The π-complex; $(1,1')\nu CH_2(s)$ and $(6,6')\nu C{=}C/CH_2$ scissors. The ethylidyne complex; $(4.4')\nu CH_3(s)$, $(5.5')\delta CH_3$ overtone and $(8.8')\delta CH_3(s)$. The di-σ-adsorbed complex (provisional assignment); $(3.3')\nu CH_2(s)$ and $(7.7')\delta CH_2$ scissors. *n*-Butyl dimerized species (provisional assignment; Morrow & Sheppard 1969)) $(2,2')\delta CH_3(as)$. A second species also contributes to bands (4.4′).

suggests that some of the sites giving rise to this type of species on the surface of the finely divided catalyst are different from those on the most symmetrical crystal planes.

The occurrence of a strong *ca.* 1340 cm^{-1} absorption in the above spectra, and in those published by Soma (1976, 1979), had earlier been difficult to account for. However, it is now identified as arising from the then-unexpected but now well characterized CH_3CM_3 (ethylidyne) surface species. Soma (1979) had previously shown that the π-complex absorptions are more prominent at low temperatures (*ca.* 195 K) but convert into the species giving the *ca.* 1340 cm^{-1} band as the temperature rises, just as has been described above from the e.e.l. spectra on Pt(111). Some recent spectra from ethylene on Pt–SiO_2 taken at low coverage (McDougall 1985) show that the strong νCH *ca.* 2890 cm^{-1} absorption on Pt may only partially be accounted for by the presence of this ethylidyne species. The assignments to the di-σ-adsorbed complex are based on those of the model compound shown in figure 6, although it is not yet clear whether the second component to the absorption at 2890 cm^{-1} band should alternatively be assigned to the CH-stretching frequency of this complex allowed under the metal-surface selection rule (Pearce & Sheppard 1976).

It is seen that the finely divided metal catalyst – which is closely related to a 'working' catalyst – does not show the presence of a single chemisorbed species from ethylene but rather the presence of at least four different ones. Two of these have been observed to contribute at different rates to catalytic hydrogenation (Prentice *et al.* 1976; Soma 1979). It was reported that addition of hydrogen to this mixture of adsorbed species leads rapidly to the removal of the bands from the π-complex, but much more slowly to those of the now-identified ethylidyne species. This finding is as would be expected as the ethylidyne complex is formed by hydrogen removal from π-adsorbed species.

Similar spectra were obtained in this laboratory (McDougall 1985) from ethylene on another finely divided Pt catalyst prepared by the reaction of silica with $Pt(NH_3)_4Cl_2$ and $Pt(NH_3)_4(OH)_2$ and reduction in hydrogen at 400 °C. This procedure gives a very well characterized 6% Pt (by mass) catalyst (EUROPT-1), which has a very uniform distribution of metal particles of approximate diameter 2 nm (Wells 1981). A modified procedure with a Pd catalyst, involving a reduced evacuation period of one hour at 400 °C after hydrogen reduction instead of the normal overnight evacuation, led to a markedly different infrared spectrum. Absorption bands from a new species occurred in the latter spectrum, tentatively identified as a di-π-adsorbed species of formula $M(C_2H_2)M$ with the CC bond perpendicular to the MM direction (James & Sheppard 1982).

6. CONCLUSIONS

6.1 *Spectral interpretations*

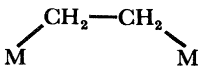
The spectra illustrated in figures 3–7 show that e.e.l.s. can be very effectively used to obtain good results even from relatively weak spectra such as those from adsorbed hydrocarbons. Figures 5–7 show how these spectra can be well interpreted in terms of the structures of the chemisorbed species from which they originate. This is particularly so when on-specular e.e.l. spectra of the surface complexes are compared with the infrared spectra of model cluster compounds of known structures for appropriate ligands. Figure 8 shows that the interpretation of the more complex multi-site spectra from a hydrocarbon such as ethylene adsorbed on finely divided metal catalysts can be greatly helped by the e.e.l. results from the simplified metal single-crystal spectra. The view that the spectra from the metal single crystals, obtained necessarily under high vacuum, are of little relevance to those obtained in catalysts, which is sometimes asserted, is therefore seen to be not generally justified. In this case, and probably in many others, the relevance is a real one in that the results obtained for the simplified single-crystal work help a great deal in interpreting results from close to 'working' catalyst systems.

We conclude by collecting together the results in the surface species obtained by e.e.l.s. or reflection–absorption infrared spectroscopy on the three metals nickel, palladium and platinum (*a*) for ethylene adsorbed at low temperatures on the (111) and (110) surface planes and (*b*) for the three adsorbates carbon monoxide, ethylene and acetylene adsorbed on the (111) faces of these metals. The results obtained to date are summarized in tables 2 and 3. Together they show that the preferred chemisorbed species vary in a subtle manner with the metal, the crystal plane and the nature of the adsorbate.

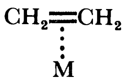
TABLE 2. A SUMMARY OF THE E.E.L.S. IDENTIFIED C_2H_4 SURFACE SPECIES FROM ETHYLENE ADSORBED ON (111) AND (110) CRYSTAL FACES OF NICKEL, PALLADIUM AND PLATINUM AT LOW TEMPERATURES

crystal face	(111)	(110)
Ni	di-σ⁽¹⁾	di-σ⁽²⁾; (π on carbided surface⁽³⁾)
Pd	π⁽⁴⁾	π⁽⁵⁾
Pt	di-σ⁽⁶⁾; (π on oxidized surface⁽¹⁾)	—

di − σ =



π =



References: (1) Lehwald & Ibach (1979); (2) and (3) Anson *et al.* 1983*a*); (4) Gates & Kesmodel (1982*a*, *b*); (5) Chesters *et al.* (1985); (6) Ibach & Lehwald (1978), Steininger *et al.* (1982).

TABLE 3. A SUMMARY OF THE SURFACE SPECIES FORMED ON THE (111) SURFACES OF NICKEL, PALLADIUM AND PLATINUM BY NON-DISSOCIATIVE ADSORPTION OF CO, C_2H_4 AND C_2H_4 AS DETERMINED BY E.E.L.S. OR REFLECTION–ABSORPTION INFRARED SPECTROSCOPY

(Notation of CO: L, linear adsorption on one metal atom; B_2, 2-fold bridged species; B_3, 3-fold bridged species. For C_2H_4, see diagrams in table 2. For C_2H_2: type A, an as yet unidentified species, possibly involving unequal interaction with the two slightly different threefold sites in the unit cell; type B, a di-σ/π-bonded species involving a triangle of metal atoms (Anson *et al.* 1983*b*).)

metal (crystal face)	CO	C_2H_4	C_2H_4
Ni(111)	$B_3 \rightarrow B_2$ (+L)⁽¹⁾	di-σ⁽⁴⁾	type A⁽⁷⁾
Pd(111)	$B_3 \rightarrow B_2$ (+L)⁽²⁾	π⁽⁵⁾	type B⁽⁸⁾
Pt(111)	$L \rightarrow L + B_2$⁽³⁾	di-σ⁽⁶⁾	type B⁽⁹⁾

References: (1) Campuzano & Greenler (1979); (2) Bradshaw & Hoffmann (1978); (3) Froitzheim *et al.* (1977), Ibach (1982); (4) Lehwald & Ibach (1979); (5) Gates & Kesmodel (1982*a*, *b*); (6) Ibach & Lehwald (1978), Steininger *et al.* (1982); (7) Ibach & Lehwald (1981); (8) Gates & Kesmodel (1982*a*, *b*, 1983); (9) Ibach & Lehwald (1978).

Considering first the results given in table 2, it might have been expected that if both the alternative di-σ-adsorbed or π-bonded species had been found on different metals that there might have been a gradual gradation of the species present from nickel towards platinum. It is seen, however, that nickel and platinum normally give the di-σ-adsorbed species whereas palladium prefers π-adsorption. This change in the adsorbed species from palladium to platinum occurs even though the metal–metal inter-nuclear distances are virtually identical, 0.275 and 0.277 nm, respectively, so that this geometrical factor is clearly not a primary determinant. A possible alternative correlation is with the somewhat different distributions of electrons between nd and $(n+1)$s electrons as the three metal atoms nickel to platinum have the outer electronic configurations $(3d)^8$ $(4s)^2$, $(4d)^{10}$ $(5s)^0$ and $(5d)^9$ $(6s)^1$ respectively. It is also of interest that the carbided nickel (110) and the oxidized Pt (111) surfaces give the π-adsorbed species instead of the di-σ one present on the clean surfaces.

In general, it seems that there is not a great stability difference between the two types of adsorption complex. Perhaps, as in the well known case of adsorbed CO (Sheppard & Nguyen 1978), differences in the readiness for synergic back-bonding from metal d-orbitals to the π*-antibonding orbital of the adsorbed ethylene acts as a driving force towards one type of adsorbed species rather than the other. The lower CC bond order in the di-σ-adsorbed species implies the presence of more back-donation. For Ni (110) an attraction of electrons by the surface carbide atoms (these are found to be atomic in form from the e.e.l. spectrum of the carbided surface), and for Pt(111) by the adsorbed oxygen atoms, might result in less back-donation and hence a preference for the alternative π-bonded species.

Table 3 demonstrates that the same (111) face of the three metals exhibit very different behaviour with respect to the three ligands and that the degree of coverage of the surface can also have important effects. With CO as ligand, Pt(111) is the odd metal in that it prefers the linear species at low coverage whereas the other two metals prefer threefold bridged species. The relative number of sites per unit mesh of the (111) surface is two for threefold (counting as the same the two slightly different sites with and without an atom in the next layer), three for twofold and one for linear (onefold) sites (Sheppard & Erkelens 1984). Although van der Waals radii of the adsorbed species are too great to anticipate a coverage of one adsorbed species per unit mesh, these statistical factors may still be of significance at the higher coverages attainable and could provide a reason for the preference of twofold bridge CO species at higher coverage in each case. The small proportion of linear sites found on Pd(111) and Ni(111) at only the highest coverages may involve random ‘fill-in’ processes at faults in the domains of adsorbed species at high coverages when l.e.e.d. shows that adsorption involves ‘out-of-register’ adsorption with respect to the metal substrate.

While with CO, Pt is the odd metal, we have already seen that with ethylene it is Pd, and table 3 shows that with acetylene it is Ni. Clearly factors associated with the adsorbates as well as with the metals control these different effects. It is seen that the chemisorption processes are very subtle, and doubtless this accounts for the great sensitivity to the metal involved in catalysis of particular reactions. At present, we are beginning to obtain systematic experimental evidence from vibrational spectroscopy with the help of which these problems can be addressed. In effect, it seems that the different adsorbates can be considered as probes of different sizes, shapes and electron donating or accepting abilities with which to explore the electronic structures and reactivities of metal surfaces.

6.2 *Experimental considerations*

There is no question that the high sensitivity of e.e.l.s. has opened up the field of the vibrational spectra of adsorbed species in a very advantageous way, as described. The method has, however, some compensating disadvantages in comparison with the photon-based spectroscopies.

One of the disadvantages concerns the resolution attainable by e.e.l.s., which, with acceptable signal to noise ratio, is about 3 meV (*ca.* 25 cm^{-1}) at best. By contrast, infrared spectroscopy applied to samples in condensed phases can readily obtain resolutions of 1 cm^{-1} (*ca.* 0.125 meV). In the context of electron spectroscopy, e.e.l.s. is sometimes qualified with the phrase 'high-resolution' and the abbreviation h.r.e.e.l.s. is often used. This prefix is a misnomer as far as the photon vibrational spectroscopies are concerned and is therefore best avoided. If a distinction needs to be made from electron energy loss spectroscopy of lower resolution used in the context of electronic spectroscopy, an alternative description could be vibrational electron energy loss spectroscopy or v.e.e.l.s. Little disadvantage may result from the use of the lower resolution of e.e.l.s. in comparison with infrared spectroscopy to study the vibrational spectra of relatively simple molecular species, which give rise to few energy losses. Although the disadvantages clearly become more pronounced in studying the complex spectra from larger adsorbed species, which at low resolution will give rise to overlapping absorptions, the patterns of spectra can still expect to be usefully distinguishable. For example, the di-σ-adsorbed species from 1-butene and *cis*- and *trans*-2-butenes on Pt(111) can readily be distinguished (N. R. Avery and N. Sheppard, unpublished work).

Whereas any experimental work on single-crystal surfaces, necessarily of low area, requires the use of ultra-high vacuum (*ca.* 10^{-10} mbar), for e.e.l.s. there is also a limit of about 10^{-6} mbar to the pressure of gas phase that can be in contact with the surface. On the other hand, in infrared spectroscopy the effective limit is set by the pressure that can be accommodated by the infrared cell up to the stage that gas-phase adsorptions obscure important regions of the spectra of adsorbed species. Pressures of tens of atmospheres have been used in some cases. This is an important advantage of infrared spectroscopy, since catalytic processes often occur at higher pressures. Under such conditions more weakly adsorbed species may be of catalytic importance. Nevertheless, e.e.l.s. will normally be capable of identifying strongly chemisorbed species, and often at least one such species plays a role in a catalytic mechanism. The Langmuir–Hinshelwood mechanism envisages surface reaction as occurring between pairs of chemisorbed species; the Rideal–Eley mechanism as involving some chemisorbed and some physisorbed species. The latter type of processes would be more effectively studied by infrared spectroscopy, but the former type is also of widespread interest and amenable to powerful investigation by e.e.l.s. because of the sensitivity of this electron spectroscopic technique.

Two of us (M.A.C. and N.S.) were supported by S.E.R.C. for the work on e.e.l.s.; N.S. also benefited from an S.E.R.C. Senior Fellowship 1979–1983.

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Discussion

J. Wong (*Department of Physical Chemistry, Cambridge University, U.K.*). At high coverages of adsorbates on metal, CO on Ni(100) for example, does Professor Sheppard observe site group or factor group splitting of molecular modes classically known in molecular solids, or solids containing molecular ions like KNO_3?

N. Sheppard. Site-group symmetry effects have been observed by vibrational electron energy loss spectroscopy, for example for benzene on a variety of metal surfaces. Factor group splittings are undoubtedly present but the limited resolution of e.e.l.s. rarely allows these to be observable.

Reflection–absorption infrared spectroscopy, with its higher resolution capabilities, is much more likely to be successful in observing such effects in the future.

G. C. Bond (*Department of Chemistry, Brunel University, Uxbridge, U.K.*). It seems probable that, as one increases the temperature with any hydrocarbon–metal system, one traverses the same sequence of structures: only the temperature at which a particular structure predominates will be characteristic of the metal. The detection of the π-alkenic form of ethene on palladium may therefore simply reflect the choice of a temperature at which this form is stable.

With respect to the readier detection of such a form on surfaces partly covered by carbide or sulphur, this observation might have a geometric explanation. The π-alkenic structure probably requires only a single metal atom, while the di-σ-adsorbed state requires at least two: on a partly poisoned surface there will be many more single atoms than pairs of free metal atoms, and so the π-alkene should naturally be the preferred form.

N. Sheppard. The substantial number of results to date do not support the interesting idea that the form of non-dissociative adsorbed species from ethylene on a single-crystal metal surface depends on the temperature range studied, for example that the π-alkenic species might occur at low temperatures and the di-σ-adsorbed species at higher temperature, or vice versa. The findings to date, from the lowest temperature up to temperatures of conversion of adsorbed species to dissociative adsorbed forms, show that the same species (π-alkenic or di-σ-adsorbed ethylene) is retained in each specific case.

Professor Bond's suggested explanation for the observation of the change from di-σ-adsorbed species on certain clean metal surfaces, to π-alkenic species after pre-adsorption of oxygen or carbon, is also of interest. In my paper I suggested that this change could be related to the electron-withdrawing power of the co-adsorbates, leading to reduced back-donation to the π-antibonding orbital of the adsorbed ethylene and hence to a more nearly C=C double-bond character for the adsorbate. Your suggestion, that the partial coverage by the co-adsorbate would lead to the availability of reduced numbers of pairs of surface metal sites necessary for di-σ-adsorption, does provide a reasonable alternative explanation, and suggests the merit of further coverage-dependent co-adsorbate studies of this phenomenon.

Although the results to date suggest that at low temperatures ethylene recognizably forms either the π-complex or the di-σ-adsorbed species, there are considerable frequency differences within each category in different examples. I would not be surprised if, in the future, a continuity of structures between these two extremes were to be observed, for example of a form approximating to a metallocyclopropane structure.

M. W. Roberts (*Department of Chemistry, University College, Cardiff, U.K.*). Has the spectrum of ethylene adsorbed on clean silver been observed? If so how does it compare with that with the oxidized surface. Surface oxygen is known to modify the catalytic reactivity of silver surfaces to hydrocarbons and I wondered how this might be manifested in the adsorbed state.

N. Sheppard. To my knowledge no e.e.l. spectrum from ethylene on clean surfaces has been observed so that it is not yet possible to make this comparison.

J. T. Yates, Jr (*University of Pittsburgh, U.K.*). There are about 30 papers in the scientific literature concerned with the production of the ethylidyne species on single-crystal surfaces

(Pt(111), Pd(111), Rh(111), Ru(001)). We have been successful in producing ethylidyne on Pd–Al_2O_3 surfaces from both C_2H_4 and C_2H_2. The $\delta(CH_3)$ mode at 1333 cm^{-1} is moderately strong and can be studied with ease, while both ν_{C-C} at 1088 cm^{-1} and $\nu_s(CH_3)$ 2867 cm^{-1} are weaker in i.r. intensity. I am pleased to see that Professor Sheppard has also been able to observe this species on high-area metal preparations, and that there is general agreement with the work on single-crystal substrates in both investigations.

Reference

Beebe, T., Albert, M. & Yates, J. Jr. 1985 *Catalysis* (Submitted.)

N. Sheppard. I am glad to hear that we agree on the interpretation of the *ca.* 1340 cm^{-1} band as arising from the $\delta(CH_3)$s mode of ethylidyne derived from ethylene adsorbed at room temperature on oxide-supported metal catalysts. We have observed such absorptions on Pt, Pd and Rh supported on silica. Pearce (1974), on Rh, Prentice (1977), on Pt, and Soma (1979), on Ni, Pd and Pt (see references in my paper), had previously observed such absorptions, but at that time the interpretation was obscure without the more recent single-crystal work by e.e.l.s.