Commentary on High-Resolution Electron Energy Loss Spectroscopy

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Commentary on high-resolution electron energy loss spectroscopy

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Vibrational spectroscopy has made an increasingly important contribution to surface science in recent years. Transmission infrared absorption spectroscopy was the first spectroscopy to be applied to adsorbates (Little 1966; Hair 1967), and it remains one of the best methods for the investigation of surface species on finely divided catalyst materials. However, the development of techniques suitable for single-crystal surfaces was essential for fundamental studies of surface vibrations. Reflection–absorption infrared spectroscopy of surface layers on metal single crystals (Hoffmann 1983) is demanding in sensitivity and spectral range, although the latter has been helped by Fourier transform methods (Baker & Chesters 1982). On the other hand, high-resolution electron energy loss spectroscopy (Ibach & Mills 1982) combines high sensitivity with a very wide spectral range, and the existence of the short-range impact scattering mechanism in addition to long-range dipole scattering makes it possible to observe many more vibrational modes than those accessible to optical methods in which the surface normal selection rule is severely restrictive. The power of electron energy loss methods has stimulated intense interest in all aspects of surface vibrational spectroscopy, an interest that is reflected by a series of international conferences devoted exclusively to this theme. The preceding papers in this Discussion Meeting illustrate the continuing vigour and development of high-resolution electron energy loss spectroscopy.

The merits of the various methods for surface vibrational spectroscopy have been discussed by Professor Ibach. Infrared spectroscopy can be used at pressures up to atmospheric or higher, a particular advantage for the *in situ* study of surface species present in catalytic reactions, and while the resolution of electron energy loss has been steadily improved to a current value of about 2 meV, the superior resolution of infrared methods has much value for the study of band shapes and their broadening or splitting with changes of coverage and temperature. The detection of some of these effects is already possible by electron energy loss.

Temperature-dependent line broadening is very marked for the CO stretching band of carbon monoxide chemisorbed on bridging sites on some metals. Hayden & Bradshaw (1983) discussed the effect in terms of anharmonic coupling with a low-frequency, thermally excited frustrated-translation mode. Their striking results for CO on Pt(111) show fluxional behaviour between two-fold and three-fold bridging sites. Similar behaviour has been reported recently for CO on Cu(111) at very low temperatures (Hayden *et al.* 1985). Broadening on Ni(111), attributed to the same kind of anharmonic coupling, has been discussed by Trenary *et al.* (1984) in terms of dephasing (Gadzuk & Luntz 1984). Similarly Tully *et al.* (1985) conclude that the temperature-dependent linewidth of the Si–H stretching mode on Si(100) arises from pure dephasing, largely due to anharmonic coupling with the bending mode. Such line-broadening effects may provide an experimental link with surface reaction pathways.

The higher resolution of infrared spectroscopy is also valuable for the study of coverage-dependent frequency shifts and for the distinction between the contributions of dipole coupling and chemical (through metal) interactions with the help of isotopic mixtures (Crossley & King 1980; Hollins & Pritchard 1980). Dipole coupling can cause disproportionate intensity in bands because of molecules adsorbed at a minority of defect sites on a stepped surface (Hollins *et al.* 1984). The understanding of such effects is important for the proper interpretation of transmission spectra from supported catalysts (Hollins 1985).

The pressure limitation is one that electron energy loss spectroscopy shares with many other techniques. A partial solution is provided by the approach introduced by Somorjai (see, for example, Koel *et al.* 1984), in which the ultra-high vacuum system is provided with a means of isolating the crystal within a sealed enclosure to which gases can be introduced at high pressures. Reactions can then proceed with product monitoring by gas chromatography or mass spectrometry before pumping away the gases and returning the crystal to ultra-high vacuum conditions for analysis of remaining surface species. This approach has provided valuable results. Erley *et al.* (1983) investigated the products of Fischer–Tropsch synthesis reactions of H_2/CO mixtures at 1 atm (101325 Pa) over Fe(110). Energy loss spectra showed bands characteristic of CH and CH_2 groups. McBreen *et al.* (1984) have pursued this further, showing that CH_2 is a rather stable species that can react with carbon to form a vinylidene group CCH_2. Koel *et al.* (1984) have studied the important ethylidyne species that results from ethylene adsorption in several metals. Ethylidyne on Rh(111) exhibits a remarkable stability towards hydrogen at 1 atm and 310 K. Hydrogenation does not occur, but hydrogen–deuterium exchange takes place, slowly on a saturated layer but rapidly at lower coverages.

The major contribution of electron energy loss spectroscopy to the solution of chemical problems is well illustrated by Professor Sheppard's paper on ethylene and acetylene adsorption. Such a diversity of surface species can be generated by adsorption of a simple hydrocarbon, that it is not surprising that early attempts to account for ethylene adsorption and hydrogenation generated considerable controversy. Traditional methods yielded only fragmentary evidence for the nature of the adsorbed layer, and interpretations were many. Dissociative adsorption, associative adsorption, σ-bonding and π-bonding were all proposed. What Professor Sheppard has shown is the importance of observing a wide spectral range and establishing patterns of behaviour for a variety of surfaces over a range of temperatures coupled with a theory-based appreciation of the factors affecting relative band intensities (Sheppard & Erkelens 1984). It is now clear that even the low-temperature non-dissociative adsorption of acetylene can occur with different patterns of relative band intensities depending on local site geometries. Furthermore, confidence in the assignment of the spectra to specific surface species may be greatly strengthened by comparison with the spectra of model molecular complexes; ethylidyne is an excellent example.

Professor Ibach and Professor Mills have given further evidence for the scope of electron energy loss spectroscopy compared with optical methods. Because of the momentum transfer available from electron scattering, measurements are not limited to the centre of the surface Brillouin zone and the surface phonon band structure may be mapped out. This is a major achievement, made possible by the complementary development of experimental techniques for high-resolution loss measurements with relatively high-energy incident electrons and of very accurate theoretical predictions of the energy dependence of the scattering cross section for specific surface phonons. The observation of the S_6 mode of Ni(001) illustrates this admirably. It is also a very striking consequence of the power of this approach that theory and experiment for a specific ordered overlayer structure can be reconciled only for rather precisely defined adsorbate substrate separations, so that structural conclusions may be drawn too.

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