

ELECTRON ENERGY LOSS SPECTROSCOPY

INTRODUCTION

In **electron energy loss spectroscopy** (EELS) a material is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Inelastic interactions include phonon excitations, inter and intra band transitions, plasmon excitations, inner shell ionizations, and Cerenkov radiation. The inner-shell ionizations are particularly useful for detecting the elemental components of a material. For example, one might find that a larger-than-expected number of electrons comes through the material with 285 eV (electron volts, a unit of energy) less energy than they had when they entered the material. It so happens that this is about the amount of energy needed to remove an inner-shell electron from a carbon atom. This can be taken as evidence that there's a significant amount of carbon in the part of the material that's being hit by the electron beam. With some care, and looking at a wide range of energy losses, one can determine the types of atoms, and the numbers of atoms of each type, being struck by the beam. The scattering angle (that is, the amount that the electron's path is deflected) can also be measured, giving information about the dispersion relation of whatever material excitation caused the inelastic scattering

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CHEMISTRY: EELS

EELS: Energy Loss Spectrometry

is the study of the vibrational motion of atoms and molecules on and near the surface by the analysis of the energy spectrum of low-energy electrons backscattered from it. An electron passing through material can interact with electron clouds of the atoms present and transfer some of its kinetic energy to them. There are three kinds of EELS, they are:

1. High Resolution Electron Energy Loss Spectroscopy (HREELS)
2. Electron Energy Loss Spectroscopy (EELS)
3. Core Electron Energy Loss Spectroscopy (CEELS)

EELS - uses electrons from 0.1 to 10 keV and passes them through a thin foil of the material of interest. At high energies, the transmitted beam contains **inelastically scattered electrons** whose energy has been decreased by amounts corresponding to characteristic absorption frequencies in the solid. At lower energies, the reflected beam is monitored for the same transitions. Bulk and surface plasmons are the principal features of these spectra.

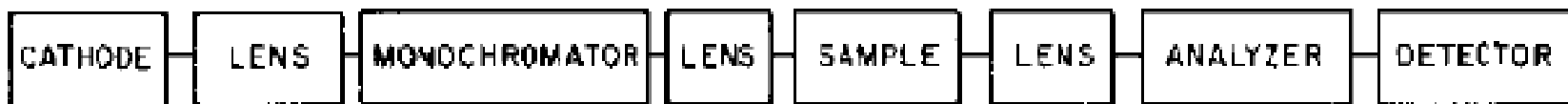
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What we can learn from it?

Electrons with energy in the range of a few electron volts sample only a few atomic layers. As they approach or exit from the crystal, they interact with the vibrational modes of the crystal surface, or possibly with other elementary excitations localized there. The energy spectrum of electrons back-reflected from the surface is thus a rich source of information on its dynamics; as we know from the well-developed fields of vibrational spectroscopy of molecules and solids, the dynamical properties of an entity, along with selection rules, offer insight into its basic structural features. Also, the vibrational modes of molecules adsorbed on the surface provide one with direct information on the nature of the chemical bonds between the molecule and the substrate.

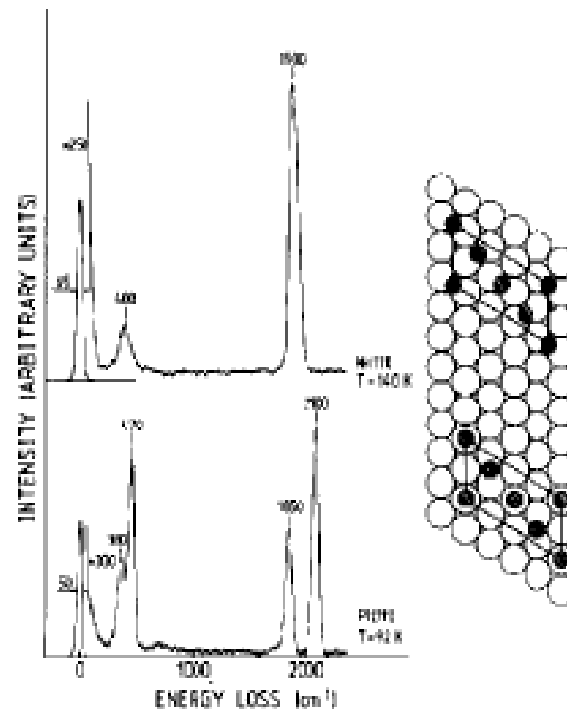
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Main parts of the instrument:



Block diagram of an electron energy loss spectrometer.

Representation of the results:



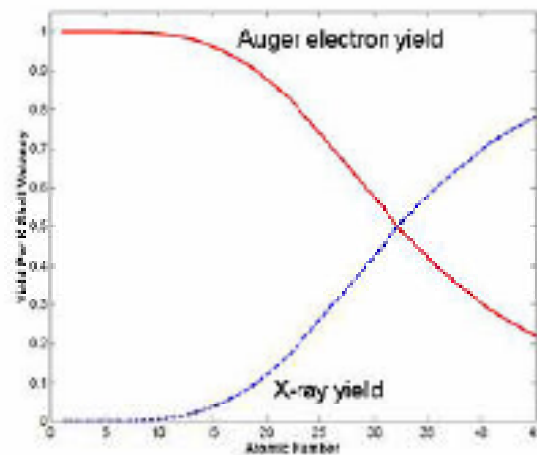
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EELS: Problems

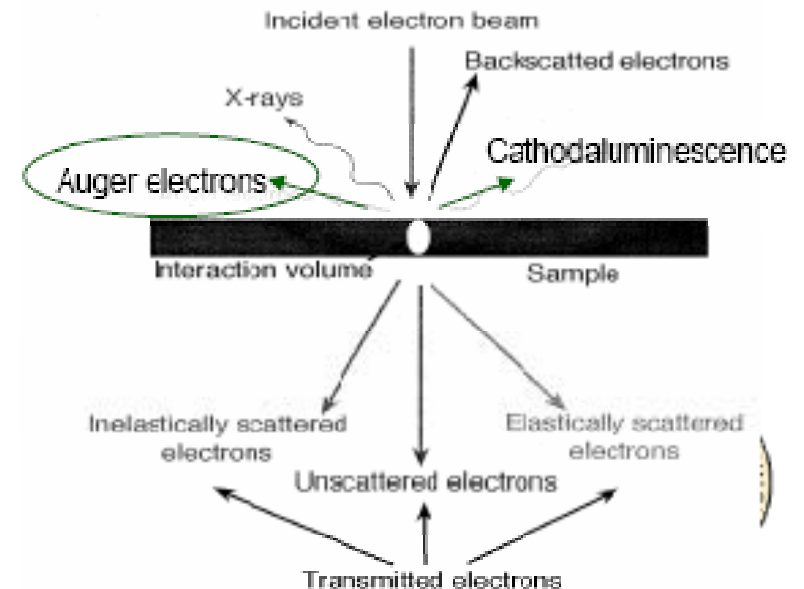
- 1) You can really interpret it only if it is single scattering → needs very thin specimens
- 2) Presence of plasmons (longitudinal wave-like oscillations of weakly bound electrons). These effects are dominant in materials with free electron structure (i.e. Li, Na, Mg, Al, ...)
- 3) Very difficult to align and very expensive

AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy (AES) is a common analytical technique used specifically in the study of surfaces. Surface sensitivity in AES arises from the fact that emitted electrons usually have energies ranging from 50 eV to 3 keV and at these values, electrons have a short mean free path in a solid. The escape depth of electrons is therefore localized to within a few nanometers of the target surface, giving AES an extreme sensitivity to surface species. Due to the low energy of Auger electrons, most AES setups are run under ultra-high vacuum (UHV) conditions



http://en.wikipedia.org/wiki/Auger_electron_spectroscopy



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History

The technique was developed by [James Hillier](#) and RF Baker in the mid 1940s but was not widely used over the next 50 years, only becoming more widespread in research in the 1990s due to advances in microscope instrumentation and vacuum technology. With modern instrumentation becoming widely available in laboratories worldwide, the technical and scientific developments from the mid 1990s have been rapid. The technique is able to take advantage of modern aberration-corrected probe forming systems to attain spatial resolutions down to ~ 0.1 nm, while with a monochromated electron source and/or careful deconvolution the energy resolution can be 100 meV or better. This has enabled detailed measurements of the atomic and electronic properties of single columns of atoms, and in a few cases, of single atoms.

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EELS and EDX

EELS is often spoken of as being complementary to [energy-dispersive x-ray spectroscopy](#) (variously called EDX, EDS, XEDS, etc.), which is another common spectroscopy technique available on many electron microscopes. EDX excels at identifying the atomic composition of a material, is quite easy to use, and is particularly sensitive to heavier elements. EELS has historically been a more difficult technique but is in principle capable of measuring atomic composition, chemical bonding, valence and conduction band electronic properties, surface properties, and element-specific pair distance distribution functions. EELS tends to work best at relatively low atomic numbers, where the excitation edges tend to be sharp, well-defined, and at experimentally accessible energy losses (the signal being very weak beyond about 3 keV energy loss). EELS is perhaps best developed for the elements ranging from carbon through the 3d transition metals (from scandium to zinc). For carbon, an experienced spectroscopist can tell at a glance the differences among diamond, graphite, amorphous carbon, and "mineral" carbon (such as the carbon appearing in carbonates). The spectra of 3d transition metals can be analyzed to identify the oxidation states of the atoms. Cu(I), for instance, has a different so-called "white-line" intensity ratio than does Cu(II). This ability to "fingerprint" different forms of the same element is a strong advantage of EELS over EDX. The difference is mainly due to the difference in energy resolution between the two techniques (~1 eV or better for EELS, perhaps a few times ten eV for EDX).

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Variants

There are several basic flavors of EELS, primarily classified by the geometry and by the kinetic energy of the incident electrons (typically measured in kiloelectron-volts, or keV). Probably the most common today is transmission EELS, in which the kinetic energies are typically 100 to 300 keV and the incident electrons pass entirely through the material sample. Usually this occurs in a transmission electron microscope (TEM), although some dedicated systems exist which enable extreme resolution in terms of energy and momentum transfer at the expense of spatial resolution.

Other flavors include reflection EELS (including reflection high-energy electron energy-loss spectroscopy (RHEELS), typically at 10 to 30 keV) and aloof EELS (sometimes called near-field EELS, in which the electron beam does not in fact strike the sample but instead interacts with it via the long-ranged Coulomb interaction; aloof EELS is particularly sensitive to surface properties but is limited to very small energy losses such as those associated with surface plasmons or direct interband transitions).

Within transmission EELS, the technique is further subdivided into valence EELS (which measures plasmons and interband transitions) and inner-shell ionization EELS (which provides much the same information as x-ray absorption spectroscopy, but from much smaller volumes of material). The dividing line between the two, while somewhat ill-defined, is in the vicinity of 50 eV energy loss.

High resolution electron energy loss spectroscopy, in which the electron beam is 1eV to 10eV, and highly monochromatic

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Thickness measurements

EELS allows quick and reliable measurement of local thickness in transmission electron microscope.[\[1\]](#) The most efficient procedure is the following:[\[2\]](#)

Measure the energy loss spectrum in the energy range about -5..200 eV (wider better). Such measurement is quick (milliseconds) and thus can be applied to materials normally unstable under electron beam.

Analyse the spectrum: (i) extract zero-loss peak (ZLP) using standard routines; (ii) calculate integrals under the ZLP (I_0) and under the whole spectrum (I).

The thickness t is calculated as $mfp \cdot \ln(I/I_0)$. Here mfp is the mean free path of electron inelastic scattering, which has recently been tabulated for most elemental solids and oxides.[\[3\]](#)

The spatial resolution of this procedure is limited by the plasmon localization and is about 1 nm,[\[1\]](#) meaning that spatial thickness maps can be measured in scanning transmission electron microscope with ~1 nm resolution.

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Physics of HREELS

As mentioned above HREELS involves an inelastic scattering process on a surface. For those processes the conservation of energy as well as the conservation of momentum's projection parallel to the surface hold:

$E_i = E_s + \Delta E_k$, $|| = ks$, $|| + q || + GE$ are energies k and q are wave vectors and G denotes a reciprocal lattice vector. One should mention at this point that for non perfect surfaces G is not in any case a well defined quantum number, what has to be considered when using the second relation. Variables subscripted with i denote values of incident electrons those subscripted with s values of scattered electrons. " $||$ " denotes parallel to the surface.

For the description of the inelastic scattering processes due to the excitation of vibrational modes of adsorbates different approaches exist. The simplest approach distinguishes between regimes of small and large scattering angles:

[\[edit\]](#) Dipole scattering

Figurative interpretation of dipole scattering

The so called dipole scattering can be applied when the scattered beam is very near to the specular direction. In this case a macroscopic theory can be applied to explain the results. It can be approached using the so called dielectrical theory of which a quantum mechanical treatment was first presented by E. Evans and D.L. Mills in the early 1970s. Or by a more unformular model which exactly only holds for perfect conductors: A unit cell at the surface does not have homogenous surrounding hence it is supposed to have an electrical dipole moment. When a molecule is adsorbed to the surface there can be an additional dipole moment and the total dipole moment P is present. This dipole moment causes a long range electronic potential in the vacuum above the surface. On this potential the incident electron can scatter inelastically what means it excites vibrations in the dipole structure. The dipole moment can than be written as $P + pe/\omega t$. When the adsorbate sticks to a metal surface imaginary dipoles occur as shown in the figure on the right. Hence for an adsorbed dipole normal to the surface the dipole moment "seen" from the vacuum doubles. Whereas the dipole moment of a parallel to the surface adsorbed dipole vanishes. Hence an incident electron can excite the adsorbed dipole only when it is adsorbed normal to the surface and the vibrational mode can be detected in the energy loss spectrum. Is the dipole parallel adsorbed than no energy loss will be detected and the vibrational modes of the dipole are missing in the energy loss spectrum.

The dielectric model holds also when the material on which the molecule adsorbs is not a metal. The picture shown above is then the limit for where ϵ denotes the relative dielectrical constant. When measuring the intensity of the electron energy loss peaks and comparing to other experimental results or to theoretical models it can also be told whether a molecule is adsorbed normal to the surface or tilted by an angle. As the incident electron in this model has to be scattered in the region above the surface it does not come to a direct impact at the surface and as the amount of momentum transferred is therefore small the scattering of is very much into the specular direction.

[\[edit\]](#) Impact scattering

Impact scattering is the regime which deals with electrons that are scattered further away from the specular direction. In those cases no macroscopic theory exists and a microscopic theory like, quantum mechanical dispersion theory, has to be applied. Symmetry considerations than also results in certain selection rules (They assume that the energy lost in the inelastic scattering process is negligible):

When the scattering plane is a plane of reflection symmetry then the scattering amplitude for every ks in the scattering plane vanishes.

When the plane perpendicular to the surface and the scattering plane is a plane of reflection symmetry and time reversal symmetry holds then the scattering amplitudes in specular direction vanishes for modes whose normal coordinates are odd under the reflection.

When the axis normal to the surface is an axis of twofold symmetry, and time reversal symmetry holds then the scattering amplitudes in specular direction vanishes for modes whose normal modes are odd under the twofold rotation.

All those selection rules make it possible to identify the normal coordinates of the adsorbed molecules.

[\[edit\]](#) Intermediate negative ion resonance

Intermediate negative ion resonance: The electron forms a compound state with an adsorbed molecule during the scattering process. But the lifetime of those states are so short that this type of scattering is barely observed. All of those regimes can at once be described with the help of the single microscopic theory the selection rule find their origins that in symmetry considerations.

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What is EELS?

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CEELS - needs electrons of energy sufficient to ionize core electrons. Usually studied in the double differential mode (like AES). Signals are characteristic of atomic core energy levels.

EELS and CEELS are less common. So here we just give brief description of them, and we give a more comprehensive description of HREELS.

HREELS - This is the most important electron loss spectroscopy. A new variant, TREELS (Time-Resolved Electron Energy Loss Spectroscopy - the "high resolution" is still inferred) allows one to monitor these signals in real time to study kinetic events.

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Why do we use HREELS?

The incident electrons are of quite low energy (a few eV) and the losses are in the meV range. The primary focus of study for this technique is vibrational structure of the surface and especially of adsorbates on that surface. As such, it is a competitive technique with RAIRS. RAIRS has the advantage of significantly greater energy resolution, but HREELS can study vibrational features of energy right down to a few meV of O (depending upon the width of the incident beam

- **What we can learn from it?**

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The incoming electrons take note of the oscillating dipoles that are present on the surface. Most often these arise from the vibrational modes of the molecular adsorbates that are present. It is also aware of the chemisorption bonds to the surface. Furthermore, phonons in the surface of semiconducting substrates (not metallic) also interact with the electron beam.

Two scattering modes are observed, differentiated by the mechanism with which they scatter.

Dipole Scattering:

This is a long-range effect mediated by the Coulomb field whereby the incoming charged electron is influenced by a vibrating dipole at the surface. (as shown in below animator) Such an electron is scattered specularly with an energy loss characteristic of the energy it deposited in the vibrational mode. Hence, such information is exactly like an IR spectrum. And, as with RAIRS, the normal dipole selection rule still applies, that is that it is blind to dipoles which oscillate parallel to the surface and can only interact with dipoles perpendicular (normal) to the surface.

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Impact Scattering:

This is a short range scattering process from the ion core. The scattering is more isotropic (not in the specular direction, but rather everywhere) but the energy losses still reflect vibrational excitations in the adsorbate. The angular distribution of peaks around the specular direction can distinguish between peaks which result from different scattering modes (Dipole Scattering is dominant).

Schematic illustration of the operation of the normal dipole selection rule in HREELS. Image dipoles within the surface either enhance (for normal orientation on the left) or negate (for parallel orientation on the right) the effect of dipoles in the vacuum above the surface. There is therefore a selection rule that favors normally dipoles.

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Vibration of adsorbed Atom

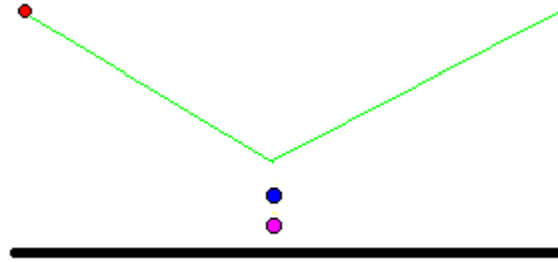
Surface vibrations are more than adsorbed molecular vibrations, when atoms adsorb on the surface, new vibrations will occur.

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Spectra:

The interpretation of HREELS spectra follows that of RAIRS. Bear in mind that RAIRS spectra are usually cast in wavenumbers while HREELS are in meV ($1 \text{ meV} = 8.065 \text{ cm}^{-1}$). The resolution in RAIRS is typically 0.25 meV while it is about 20 meV for HREELS. By comparison with the RAIRS, a spectrum of the same material taken both by RAIRS and HREELS is shown in Fig. Note the additional spectra given here, demonstrating the molecular information obtainable.

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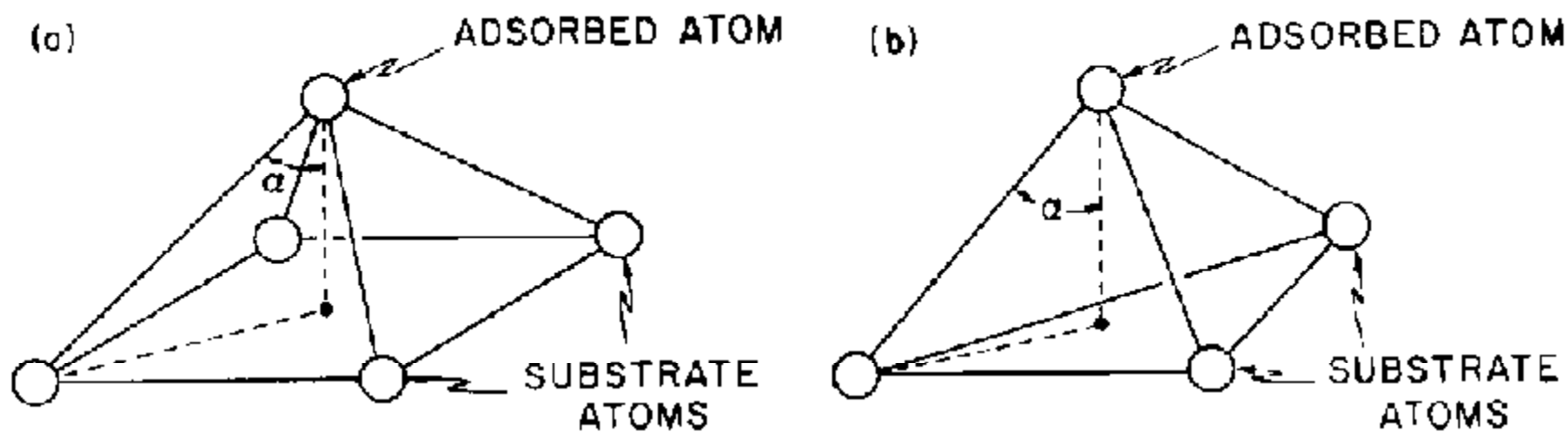
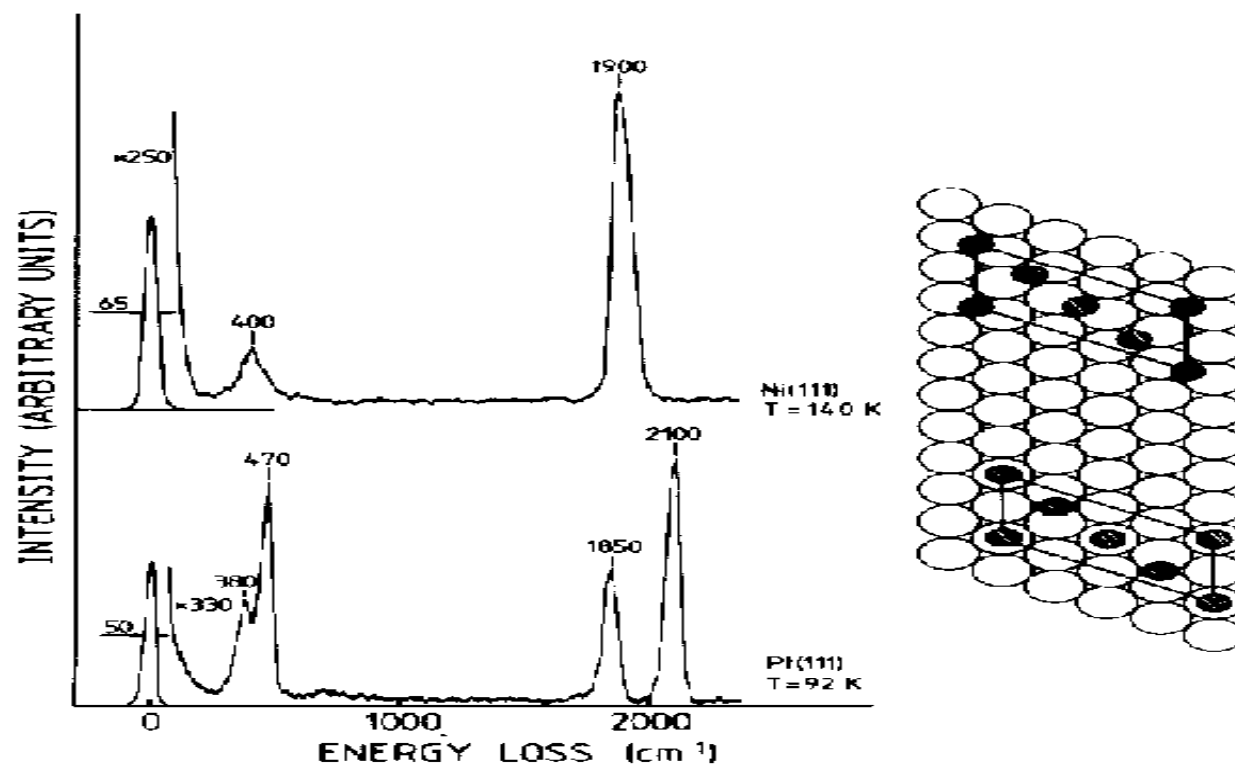


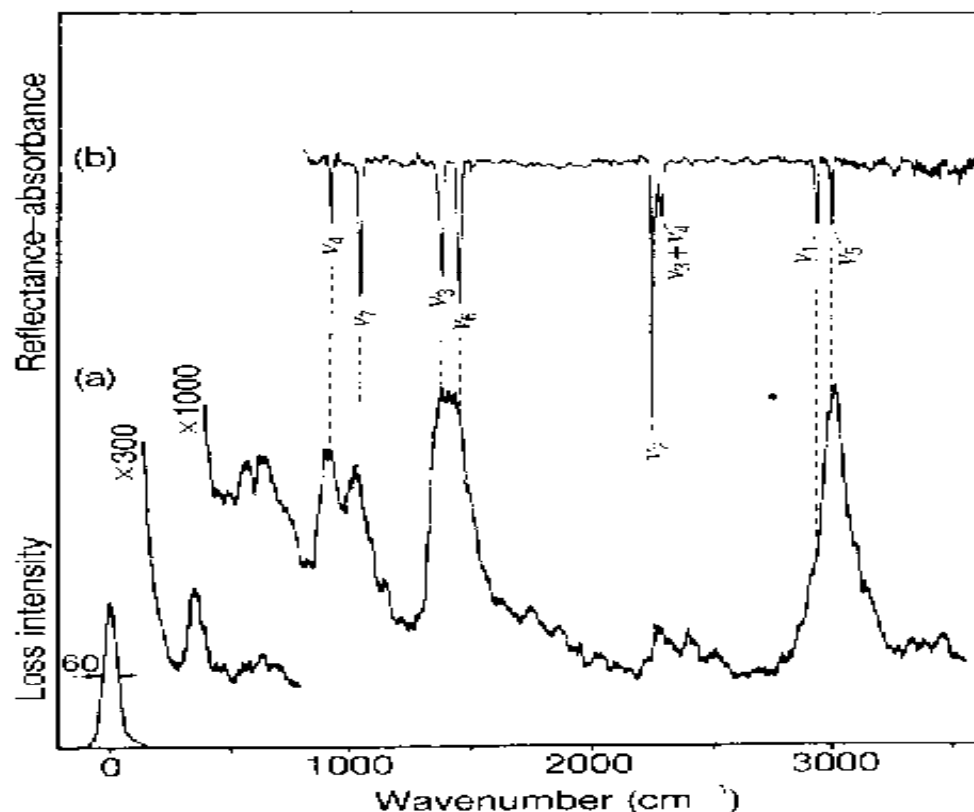
Fig. An adsorbed atom that sits on a hollow site of (a) fourfold symmetry and (b) threefold symmetry.

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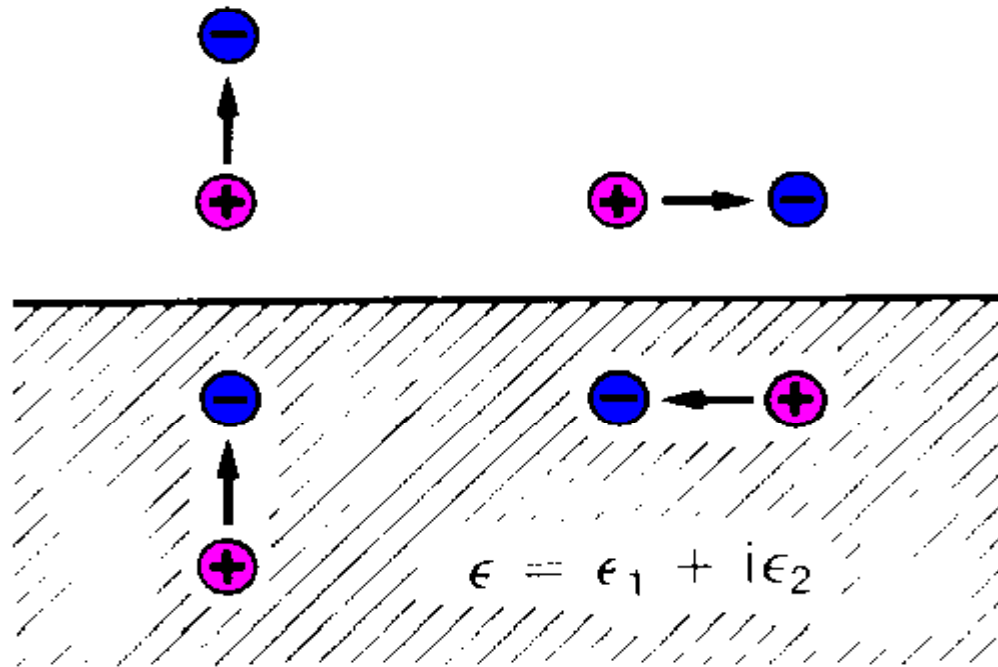
Electron energy loss spectra of the Ni(111) and Pt(111) surfaces, each covered with half a monolayer of CO which orders into a $c(4 \times 2)$ overlayer. On the nickel surface the vibration spectrum indicates only a single CO species in a site of high symmetry. The only possibility for positioning the two-dimensional CO lattice on the surface consistent with the single type of adsorption site is to place all CO molecules into twofold bridges. By similar reasoning, half the CO molecules must occupy on-top sites on the Pt(111) surface. This example shows how powerful the *in situ* comparison of vibrational spectra and diffraction pattern can be, since a qualitative structure analysis is achieved without analyzing diffraction intensities.

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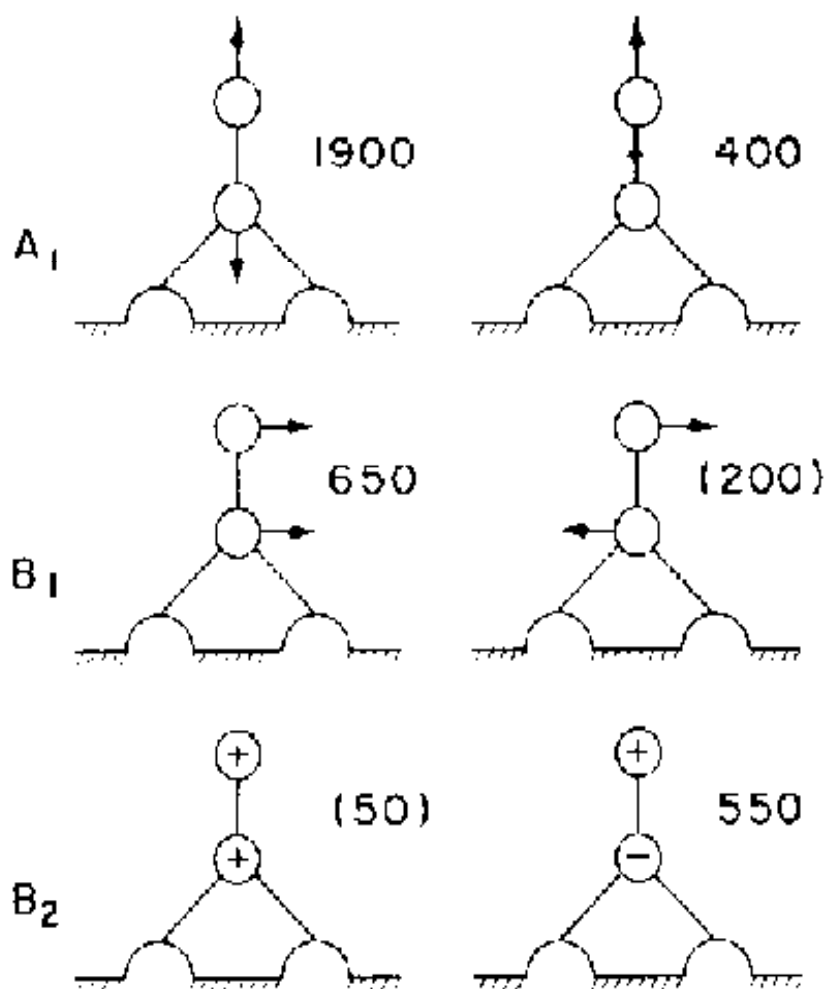


Comparison by Erley¹ of the RAIRS and HREELS vibrational spectra of acetonitrile, CH_3CN , on $\text{Cu}(111)$ at 100 K. The RAIRS spectrum (b) cuts off at $\approx 800 \text{ cm}^{-1}$, due to the frequency cut-off in the detector, whereas HREELS can be recorded to zero loss. However, the resolution in RAIRS is of the order of 2 cm^{-1} as against $\approx 60 \text{ cm}^{-1}$ in HREELS. Thus bands ν_3 and ν_6 , ν_1 and ν_5 , can be resolved by RAIRS but not by HREELS. These are the reasons why the two techniques are often used together.

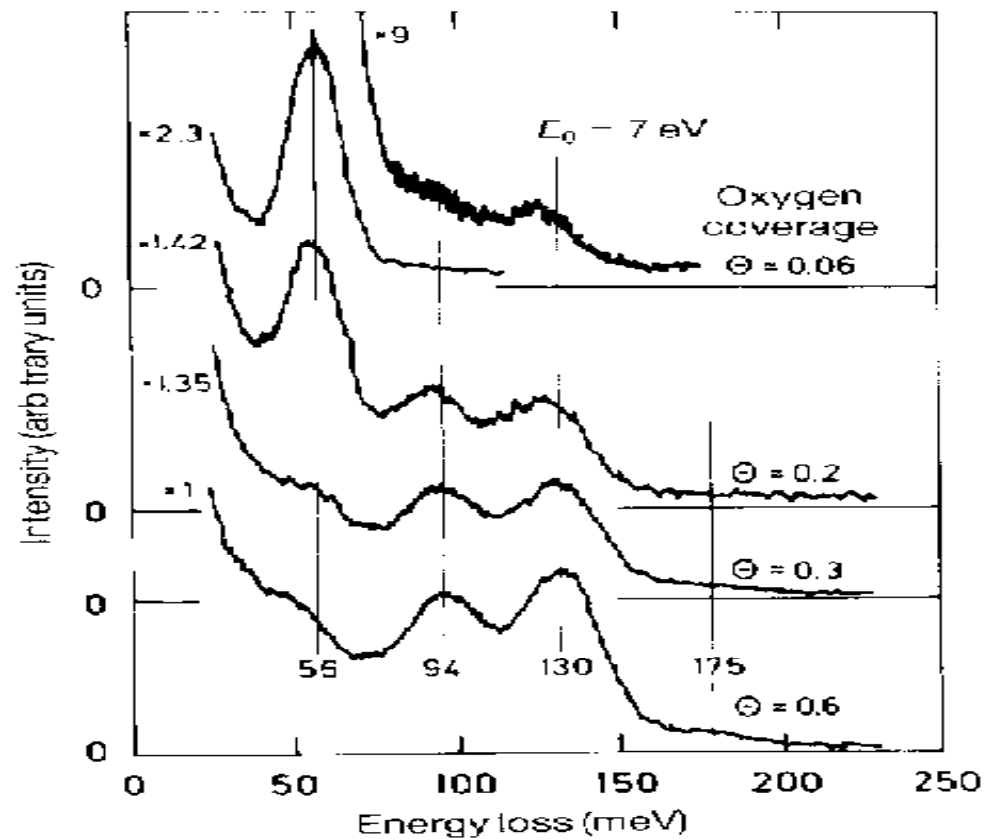
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The six eigenmodes of CO on a two fold bridging site with an assumed C_{2v} symmetry. Only the CO stretching vibration is a genuine mode of the gas-phase molecule. The rest of the surface modes are hindered translations and rotations. The frequencies (in cm^{-1}) are approximate values taken from a cluster calculation (from Richardson and Bradshaw [14], used with permission) and should be used as a guideline only. The frequencies of two modes fall into the phonon band and may therefore not be localized on the surface.



Example of a feature in a HREELS spectrum due to surface phonon scattering, from Ibach *et al.*¹⁹ The peak at 56 meV from the Si(111)-(2 × 1) surface prepared by cleavage in vacuo, at a primary energy of 5 eV, has been ascribed to such scattering. Note the rapid damping of such a peak on exposure to oxygen; $\theta = 1$ corresponds to monolayer coverage. The half-width of the loss feature is the same as that of the elastic beam, which confirms the surface origin.

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Supported Catalysts (Metal Clusters). In recent years, HREELS has been shown to be applicable to the study of catalysts consisting of small transition metal clusters supported on an oxide substrate. The surface specificity of the technique allows one to probe those vibrational modes associated with bonding of the adsorbate of interest to the small metal particles. In contrast to work on single-crystal metals, one is dealing with the following new issues: (i) possibility of electron beam charging of the oxide support; (ii) strong optical phonon modes present from the oxide; and (iii) diffuse elastic scattering due to the rougher nature of the surface. We illustrate some of these effects in a discussion of the adsorption and thermal evolution of ethylene (C_2H_4) on a model-supported platinum catalyst.⁷ These catalysts were formed by first growing a thin film of alumina by reactive Al deposition on a metal substrate in an oxygen environment. Platinum was then vapor deposited in the range of a fraction of a monolayer to several monolayers total platinum coverage to form small clusters of typical diameter 1.0–1.6 nm. Figure 3a shows the HREELS spectrum of the model catalyst before C_2H_4 adsorption. Electron beam charging was not present because of the ultrathin (several monolayers) nature of the aluminum oxide support. However, as discussed by Liehr et al.,⁸ such charging can be dealt with by a secondary electron beam. We find that the elastic scattering from these surfaces is quite diffuse, leading to specular intensity typically reduced by two orders of magnitude compared with a single-crystal surface. It has therefore been explained that impact scattering is the dominant mechanism for most adsorbate modes detected on these systems.⁷ The modes 600 and 900 cm^{-1} in Figure 3 are due to dipole-active surface optical (Fuchs-Kliewer) modes that are well known in HREELS from oxide surfaces and are only partially screened following platinum deposition in this study. The screening, however, is sufficient so that undue interference from these modes is eliminated.

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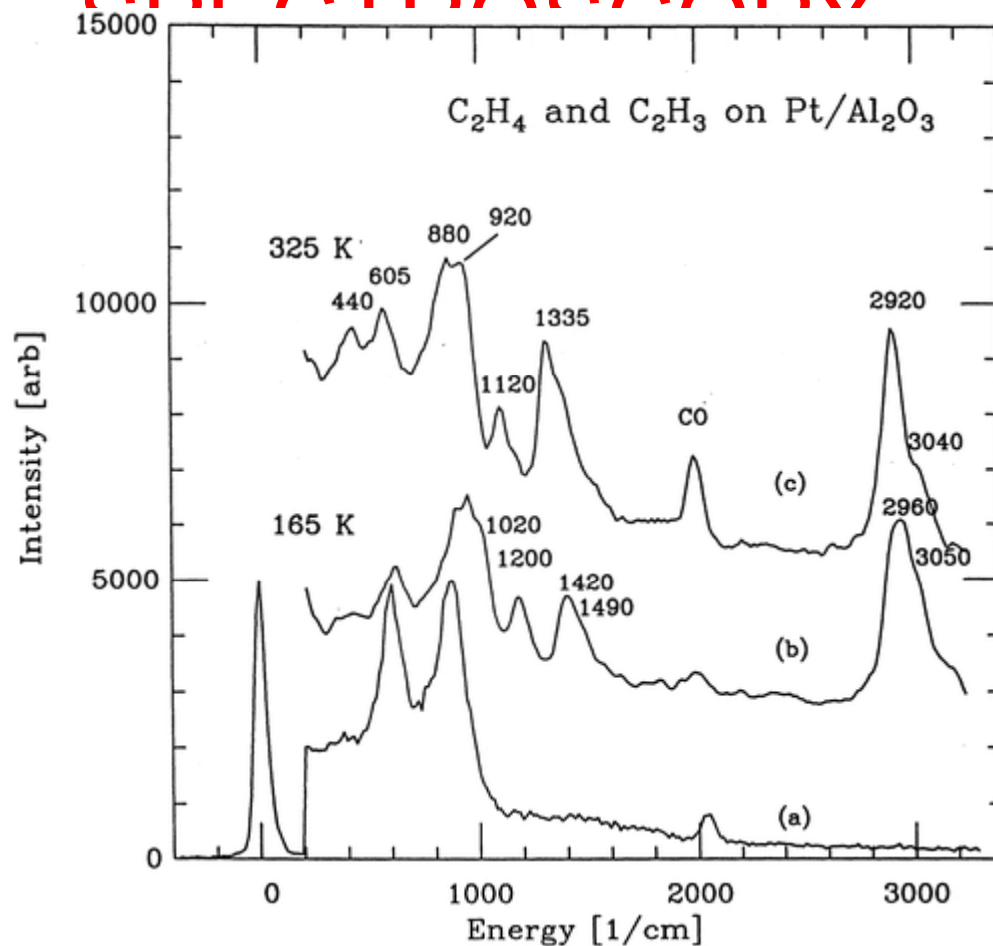


Figure 3 HREELS of ethylene on a 3.4×10^{15} atoms/cm² coverage of Pt on Al₂O₃ film: (a) clean; (b) ethylene at 165 K; (c) ethylidyne at 325 K.