Inelastic Scattering of Electrons from Adsorbate Vibrations: Large-Angle Deflections

S. Y. Tong and C. H. Li
Department of Physics and Surface Studies Laboratory, University of Wisconsin, Milwaukee, Wisconsin 53201

and

D. L. Mills
Department of Physics, University of California, Irvine, California 92717

(Received 5 September 1979)

Calculations of the energy and angle variation of large-angle, inelastic, electron scattering produced by vibrations in a $c(2\times 2)$ overlayer of CO on Ni(100) are presented. The results show pronounced structure related to the bonding site and symmetry associated with the adsorbed CO molecule. Limitations of the elementary form of the dipole-scattering formula applicable to the regime of small-angle scattering are also discussed.

During the past decade, high-resolution electron energy-loss spectroscopy (EELS) has proved a powerful means of probing vibrational motions on crystal surfaces.[1,2] With two exceptions,[3] all experiments have examined inelastic electrons which emerge very close (within 1° typically) to the specular beam. Here one expects very strong scattering confined to a narrow angular cone produced by the oscillating electric dipole moment set up by the ionic motion. The data are frequently analyzed, with apparent success, through use of an expression derived by Evans and Mills,[4] and subsequently by others.[5] From the data, coupled with theory, one may extract quantitative values for the dipole-moment effective charge (or polarizability derivative) associated with the various vibrational modes.

The dipole-scattering theory shows that this mechanism leads to an intense lobe of inelastics, confined to a cone of angular halfwidth $\psi_E = \hbar\omega_0/2E_0$ centered on the specular (and various Bragg) beams. Here E_0 is the impact energy and ω_0 the frequency of the vibration. Outside this narrow cone, where momentum transfers are on the scale of an inverse angstrom, the dipole approximation breaks down, since here the dipole term may be regarded as simply the leading term of a multipole expansion of the potential with expansion parameter of order unity. For such large scattering angles, an impact-scattering approach which emphasizes the detailed structure of the crystal potential is required, along with an explicit description of the multiple scattering of both the incoming and outgoing electrons from the adsorbate/substrate system. We report here the first set of such calculations, for vibrations in a $c(2\times 2)$ layer of CO on Ni(100). The diffraction of the electron from the adsorbate/substrate combination before and after emitting the vibrational quantum leads to pronounced structure in the energy variation of the loss intensity. Thus, large-angle EELS is a potentially rich source of information on the detailed structure of adsorbate bonding sites. In what follows, we present these calculations.

In the impact-scattering regime, with θ_0 and θ_s the angles between the incident and scattered beams and the crystal normal, respectively, and $(dP/d\Omega)$ the probability that the electron scatters into solid angle $d\Omega$, we have

$$\frac{dP}{d\Omega}=\frac{mE_0}{2\pi^2\hbar^2}\frac{\cos^2\theta_s}{\cos\theta_0}S|M(\vec{k}^{(I)},\vec{k}^{(F)};\vec{Q}_{\parallel}j)|^2. \tag{1}$$

Here m is the electron mass, S is the sample surface area, and we assume that the electron scatters from a phonon of wave vector $\vec{Q}_{\parallel}$ and polarization j in the surface layer. If, for simplicity, we ignore interactions between the molecules in calculating the vibrational spectra, then the matrix element M in Eq. (1) may be expressed in terms of the derivative with respect to nuclear displacement $\partial f(\vec{k}^{(I)},\vec{k}^{(F)})/\partial\vec{R}_{A,B}$ of the scattering amplitude $f(\vec{k}^{(I)},\vec{k}^{(F)})$ for scattering the electron from $\vec{k}^{(I)}$ to $\vec{k}^{(F)}$. We have for an AB overlayer, with the substrate treated as rigid,

$$M(\vec{k}^{(I)},\vec{k}^{(F)};\vec{Q}_{\parallel}j)=\left(\frac{\hbar}{2\omega_j}\right)^{1/2}[1+\bar{n}_j]^{1/2}\sum_{\vec{G}_{\parallel}}\delta_{\vec{k}_{\parallel}^{(F)},\,\vec{k}_{\parallel}^{(I)}-\vec{Q}_{\parallel}+\vec{G}_{\parallel}}\sum_i\left\{\frac{\sin\theta_j^{(i)}}{\sqrt{M_A}}\left(\frac{\partial f}{\partial R_A^{(i)}}\right)_0+\frac{\cos\theta_j^{(i)}}{\sqrt{M_B}}\left(\frac{\partial f}{\partial R_B^{(i)}}\right)_0\right\}, \tag{2}$$

with ω_j the normal-mode frequency, $\bar{n}_j$ the Bose-Einstein factor, $R_A^{(i)}$ the ith Cartesian component of $\vec{R}_A$, and $\theta_j^{(i)}$ a measure of the relative amplitude of nucleus A and nucleus B when normal mode j is excited. An analysis of the multiple-scattering theory allows $(\partial f/\partial R_A{}^i)_0$ to be expressed in terms of the one-particle propagator G and the T_0 matrix of the crystal.[6] If $V(\vec{r}, \{\vec{R}\})$ is the crystal potential, then we find, in notation used elsewhere,[6]

$$\left(\frac{\partial f}{\partial R_A{}^{(i)}}\right)_0 = \langle \vec{k}^{(F)} | (G + GT_0G)\left(\frac{\partial V}{\partial R_A{}^{(i)}}\right)_0 (1 + GT_0) | \vec{k}^{(i)} \rangle \quad (3)$$

which may also be arranged to read

$$\left(\frac{\partial f}{\partial R_A{}^{(i)}}\right)_0 = \langle \vec{k}^{(F)} | \psi_{\mathrm{EELS}}{}^{(i)} \rangle . \quad (4)$$

Here the outgoing EELS wave function corresponding to displacement in the ith coordinate is

$$| \psi_{\mathrm{EELS}}{}^{(i)} \rangle = g_{PE}\left(\frac{\partial V}{\partial R_A{}^{(i)}}\right)_0 | \psi_{\mathrm{LEED}}{}^{(I)} \rangle , \quad (5)$$

with $|\psi_{\mathrm{LEED}}{}^{(I)}\rangle$ the wave function constructed from LEED theory to describe the incoming electron and g_{PE} the propagator that describes the outgoing part of the wave.[7]

The quantity $(\partial V/\partial R_A{}^{(i)})$ is calculated in the present study by rigidly shifting the muffin-tin potential centered at $\vec{R}_A$. It is then possible to express matrix elements of $(\partial V/\partial R_A{}^{(i)})$ as an integral of the radial derivative $dv_A(|\vec{\rho}_A|)/d\rho_A$ of the muffin-tin potential $v_A(|\vec{\rho}_A|)$ between two radial solutions $R_l{}^{(i)}(\rho_A)$ and $R_{l'}{}^{(F)}(\rho_A)$ of the full Schrödinger equation within the muffin-tin sphere. A detailed derivation of the form we have used is presented elsewhere.[8]

Finally, we need the vibrational force constants that enter our independent-molecule model of the vibrational frequencies and eigenvectors. For CO on a site of fourfold symmetry, we have two normal modes (ω_+, ω_-) of vibration normal to the surface (C-O stretch, C-Ni mode), and four "wagging" modes parallel to the surface. Each of the latter is twofold degenerate. For each polarization, the ratio between force constants (this is all we require) can be found from the ratio ω_-/ω_+ of the frequencies. The values of ω_-/ω_+ for the perpendicular and parallel modes are taken from experimental data.[8]

In Figs. 1(a) and 1(b), we give the energy variation of the one-phonon loss cross section for the C-O stretching mode (ω_+) and the C-Ni mode (ω_-) for vibrations normal to the surface. Each has been calculated for two bonding sites, the top site (solid line) and the hollow site (dashed line).

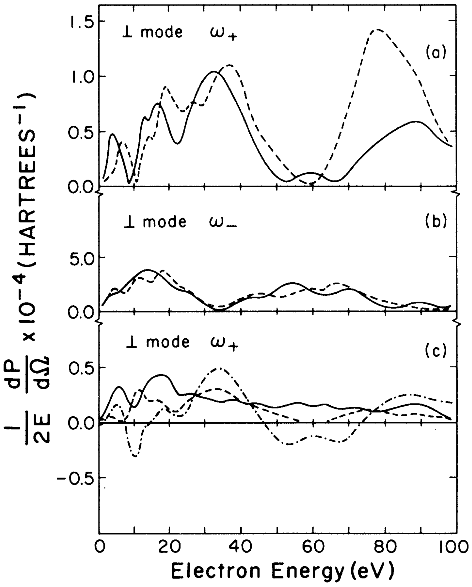

FIG. 1. Energy dependence of differential probability [in units of $1/2E$ (hartree^{-1})]. (a) and (b) $d_\perp$(Ni-C) = 1.8 Å (solid line) and 1.06 Å (broken line). (c) $d_\perp$(Ni-C) = 1.8 Å, O layer scattering (solid line), C layer scattering (broken line), and interference (chained line). $d_\perp$(C-O) = 1.13 Å, θ_0 = 30°, and θ_s = 35°.

The CO is assumed to adsorb normal to the surface with the C end down.

We see rich structure in the loss cross section from the ω_+ mode. The structure shows high sensitivity to the Ni-C spacing of the two bonding sites, and its existence is thus linked intimately to diffraction of the incident and scattered beams between overlayer and substrate atoms. Davenport, Ho, and Schrieffer[9] have studied inelastic scattering from an isolated CO molecule with axis rigidly pinned in orientation. They find a prominent negative-ion resonance of width 1.5 eV near 2 eV above vacuum. We also find a distinct peak at low energy, but we see from Fig. 1(a) that its position and intensity is influenced markedly by the Ni-C spacing. Thus, this peak has a different physical origin. Also, we find further pronounced peaks at higher energies. At the low-energy peak, our value of $(dP/d\Omega)$ is smaller than that reported by Davenport, Ho, and Schrieffer[9] by more than one order of magnitude. We believe the 11-eV inner potential of Ni removes the negative-ion resonance, and we interpret our low-energy peak as simply the first in a sequence of multiple-scattering resonances.

In Fig. 1(b), we see that there is less structure in the scattering from the C-Ni mode, though again the magnitude and energy variation of the

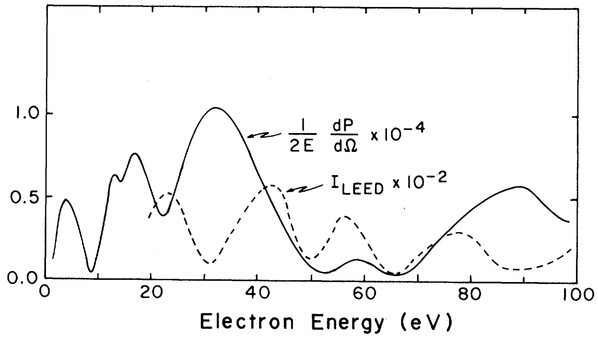

FIG. 2. Elastic specular intensity I_0 as a function of energy (broken line). $dP/d\Omega$ for ω_+ shown in Fig. 1(a) (solid line) is reproduced here. $d_\perp(\text{Ni-C}) = 1.8$ Å, $d_\perp(\text{C-O}) = 1.13$ Å, and $\theta_0 = 30°$.

loss intensity are site sensitive. From Eq. (2), one sees that each mode is described by a loss cross section that is a distinctly different synthesis of scattering-amplitude derivatives, and each may in general be expected to have its own bonding-site dependence and energy dependence. Thus, the EELS data at large-scattering angles are rich in structural information. Figure 1(c) breaks the loss intensity for the ω_+ mode with $d_\perp = 1.8$ Å into the contribution from scattering off O alone, from C alone, and from the interference between the O and C layers. The crucial role played by interference between the two layers is evident.

The small-angle dipole-scattering expression in its most elementary form[4] suggests that it is useful to plot the ratio $r(E) = I_1(E)/I_0(E)$, where $I_1(E)$ and $I_0(E)$ are the one-phonon and (elastic) specular beam intensities, respectively. In the large-angle regime, such a procedure is inappropriate. We illustrate this in Fig. 2, where we plot the energy variation of the elastic $I_0(E)$ for top-bonded CO. We see the well-known LEED IV structure in $I_0(E)$, but the structure in the phonon-loss cross section is distinctly different from that in $I_0(E)$. Thus, the ratio $r(E)$ contains no useful information: Experimentalists should provide data for $I_1(E)$ directly, except for experimental conditions where the elementary dipole form[4] is expected to be valid.

Figure 3 shows the angular variation of the loss cross section for in-plane scattering (incident wave vector, final wave vector, surface normal lie in a plane) from the stretching (ω_+) modes perpendicular (solid line) and parallel (broken line) to the surface. The parallel mode is polarized in the scattering plane, which is along [100]. The electrons are broadly distributed in angle, but note the zero on the specular for scattering from the parallel mode. This is a symmetry-dictated zero, from the combined effect of time reversal and reflection in a plane perpendicular to the scattering plane, which also contains the surface normal. The parallel mode polarized normal to the scattering plane scatters with zero intensity *whenever* $\vec{k}^{(F)}$ is swept through the scattering plane, not only along the specular. This is a consequence of reflection symmetry through the scattering plane. For adsorbates in high-symmetry sites, these zeros can be used to separate scattering from modes parallel to the surface, but parallel or perpendicular to the scattering plane.

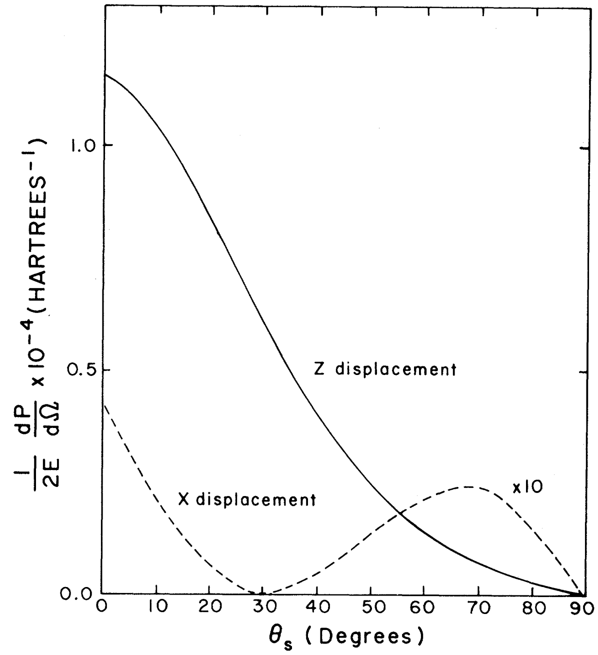

FIG. 3. Dependence of $dP/d\Omega$ [in units of $1/2E$ (hartree^{-1})] on scattering angle θ_s for CO (ω_+) modes. Displacements are normal to surface (solid line) and along [100] direction (broken line). $d_\perp(\text{Ni-C}) = 1.8$ Å, $d_\perp(\text{C-O}) = 1.13$ Å, and $E = 3.5$ eV.

At very low energies ($E_0 < 10$ eV) where many near-specular experiments are performed,[10] the physical processes are further complicated by contributions from fine-structure resonances and image-potential effects. A complete theory of even dipole scattering is thus not easy to write down. On the other hand, looking at higher energies, we note that the calculations reported in this paper show that, in the large-angle impact-scattering regime, $(dP/d\Omega)$ does not fall off with energy. Thus, if the spectrometer resolution can be maintained at higher energies, explicit contact with multiple-scattering calculations such as those reported here may prove more fruitful than attempts to interpret data taken at very low energies, especially in the absence of a more complete treatment of the dipole-scattering term.

This work is supported by the U. S. Department of Energy under Grants No. 144-N346 and No. DOE ATO3-79ER10432.

---

[1] See review articles: H. Froitzheim, in *Topics in Current Physics*, edited by H. Ibach (Springer-Verlag, New York, 1976), Vol. 4; D. L. Mills, Prog. Surf. Sci. 8, 143 (1977).

[2] H. Ibach, Phys. Rev. Lett. 41, 958 (1978); S. Andersson and J. W. Davenport, Solid State Commun. 28, 677 (1978).

[3] W. Ho, R. F. Willis, and E. W. Plummer, Phys. Rev. Lett. 40, 1463 (1978); M. R. Barnes and R. F. Willis, Phys. Rev. Lett. 41, 1729 (1978).

[4] E. Evans and D. L. Mills, Phys. Rev. B 5, 4126 (1971).

[5] D. M. Newns, Phys. Lett. 60A, 461 (1977); B. N. J. Persson, Solid State Commun. 24, 573 (1977).

[6] S. Y. Tong, Prog. Surf. Sci. 7, 1 (1975).

[7] S. Y. Tong, C. H. Li, and A. R. Lubinsky, Phys. Rev. Lett. 39, 498 (1977).

[8] C. H. Li, S. Y. Tong, and D. L. Mills, to be published.

[9] J. W. Davenport, W. Ho, and J. R. Schreiffer, Phys. Rev. B 17, 3115 (1978).

[10] E. G. McRae, J. Vac. Sci. Technol. 16, 654 (1979); R. F. Willis, B. Feuerbacher, and N. E. Christensen, Phys. Rev. Lett. 38, 1087 (1977); A. Adnot and J. D. Carette, Phys. Rev. Lett. 38, 1084 (1977).

Nonexponential Decay of Critical Concentration Fluctuations in a Binary Liquid

H. C. Burstyn, R. F. Chang,[(a)] and J. V. Sengers
Department of Physics and Astronomy, and Institute for Physical Science and Technology,
University of Maryland, College Park, Maryland 20742

(Received 17 December 1979)

By use of light scattering techniques a careful investigation has been made of the time dependence of the concentration fluctuations near the critical point of a binary liquid mixture. The experiments reveal deviations from exponential decay of these fluctuations at temperatures within 20 mdeg from the critical temperature. The observed deviations from exponential decay are in agreement with a recent theoretical prediction of Bhattacharjee and Ferrell.

This Letter is concerned with the time dependence of the order-parameter fluctuations in fluids close to the critical point. An early experimental study, made by Volochine, Bergé, and Lagues,[1] indicated that the relaxation of the concentration fluctuations of a binary liquid remained exponential even at temperatures within 3 mK from the critical temperature.[1] However, when it was established that the magnitude of the decay rate of the fluctuations was measurably affected by the critical viscosity anomaly,[2] Perl and Ferrell predicted that the memory effects in the viscosity should also induce a non-Lorentzian distortion of the Rayleigh line.[3] A possible frequency dependence of the decay rate of the order-parameter fluctuations has also been mentioned by Kawasaki and co-workers.[4,5]

A first attempt to measure the effect was made by Bendjaballah.[6] He concluded that any nonexponential decay due to the frequency dependence of the viscosity was quite small and within the resolution of his experiments. A similar conclusion was obtained by Wonica, Swinney, and Cummins[7] and, more recently, by Sorensen, Mockler, and O'Sullivan.[8] These authors were motivated by the large departure from exponential decay predicted by the dynamic droplet model, but which was not observed. The question remains whether smaller departures from exponential decay due to the frequency dependence of the viscosity can be detected experimentally.

By modifying a light scattering facility, previously constructed for an accurate determination of the static critical correlation function,[9] and cross-correlating the scattered light intensity as registered by two different photomultiplier tubes, we have *indeed* detected the presence of departures from exponential decay in the time-dependent correlation function of the concentration fluctuations close to the critical point of a binary liquid. The experimental results differ qualitatively and quantitatively from the effect