New Approach to High-Resolution Electron-Energy-Loss Spectroscopy of Polar Materials: Studies of Water and Methanol Adsorption on Ultrathin MgO(100) Films

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A novel approach to the application of high-resolution electron-energy-loss spectroscopy to polar materials is demonstrated in this Letter. By using a high-impact-energy beam and an off-specular scattering geometry, losses due to excitation of the adsorbates are observed in the 1000–4000-cm^{-1} range with little interference from the intense losses due to multiple surface optical phonons (Fuchs-Kliewer modes). Adsorption of water and methanol on ultrathin MgO(100) films on Mo(100) have been studied using this new approach.

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In the past two decades, high-resolution electron-energy-loss spectroscopy (HREELS) has become a major technique for surface vibrational studies. This technique has been generally restricted to conducting substrates (metals and semiconductors) because of surface-charging problems encountered with insulators. Only limited studies have been carried out on highly insulating surfaces, e.g., MgO(100) [1] and Al_2O_3(0001) [2]. The effects of surface charging during charged-particle measurements have been compensated or stabilized with the aid of a neutralization electron gun [3].

The difficulty associated with surface charging has been eliminated in our laboratory [4] by preparing an ultrathin, highly ordered, oxide film on the surface of a metal substrate. Any charging induced in the thin film during charged-particle measurements is dissipated via the conducting substrate. Our low-energy-electron diffraction (LEED) and surface spectroscopic studies [4] indicate that the MgO films grow epitaxially with the (100) face of MgO oriented parallel to the Mo(100) surface, and that the properties of the film are essentially identical to those of bulk, single-crystal MgO.

In the application of HREELS to adsorbates on ionic substrates, such as metal oxides, a second great difficulty encountered is that the accompanying vibrational spectra are dominated by losses due to excitation of surface optical phonons (Fuchs-Kliewer modes [5]). In the regime of small-angle inelastic scattering [6], the coupling between those surface phonons and the incident electrons is so strong that typically multiple quanta of the fundamental mode are excited. Consequently, the intense multiple phonon losses generally extend over a wide vibrational frequency range of the HREELS spectra, swamping the weak loss features of the adsorbed species (usually several orders of magnitude smaller in intensity than those of the phonons). It is then not practical to observe directly losses due to the excitation of adsorbates in the 0–4000-cm^{-1} spectral range.

Recent progress has been made in circumventing the difficulties associated with these phonon losses. For example, in order to distinguish adsorbate peaks from phonon losses, Cox *et al.* [7] have developed a Fourier-transform technique to deconvolute the phonon combination peaks from the HREELS spectrum. Very recently, this approach has been applied to the study of formic acid adsorbed on ZnO(0001) [8]. Clearly the Fourier deconvolution method is superior to simply acquiring difference spectra between clean and adsorbate-covered surfaces [7]; nevertheless, it is still basically an "indirect" technique. Of particular concern are the spurious features that may be introduced in the spectrum by the Fourier deconvolution procedure itself.

In this Letter, we report a new approach to the acquisition of HREELS data for oxides which enables the direct measurement of losses due to the excitation of adsorbed species. Utilizing a relatively high-energy-electron beam and an off-specular scattering geometry, adsorbate losses are clearly observed in the 1000–4000-cm^{-1} spectral range.

The experiments were carried out in an UHV system, described elsewhere [9], with capabilities for HREELS, Auger electron spectroscopy (AES), LEED, and for sample heating and cooling. The cleaning procedure for the Mo(100) substrate and the MgO film preparation have been presented elsewhere [4]. The HREELS measurements were carried out in the scattering compartment of a two-tiered chamber. The primary energy of the electron beam of the spectrometer can be varied between 0 and 250 eV. The spectral resolution (full width at half maximum of the elastic peak) of the data presented here was typically 80–96 cm^{-1}.

There are two mechanisms operative in the loss processes in HREELS [6]. One involves small-angle inelastic scattering (with reference to the specularly reflected beam direction) induced by long-range dipolar fields generated either by adsorbate vibrations or by surface atomic vibrations. The second is the impact-scattering mechanism which involves large-angle electron deflection (with reference to the specularly reflected beam direction). Although a fully microscopic quantum theory is required to describe the large-angle inelastic scattering process, HREELS features related to small-angle inelastic scattering can be interpreted semiclassically within the framework of the so-called dielectric theory. Accordingly, the general theory for dipolar scattering has been formulated [6,10]. The energy-loss probability Γ, describing the single event corresponding to either the excitation or emission of one surface optical phonon, is given by [10]

$$\Gamma(\omega)=\frac{4e^2}{\pi^2\hbar V_\perp}\int d^2k\frac{1}{k^2}\frac{(kV_\perp)^3}{[(\omega-\mathbf{k}\cdot\mathbf{V}_\parallel)^2+(kV_\perp)^2]^2}\times\mathrm{Im}\frac{-1}{\epsilon(\omega)+1}\,.$$

Here the integration is performed over a region defined by the angular acceptance of the energy analyzer, where $\mathrm{Im}(-1/[\epsilon(\omega)+1])$ is the loss function for surface excitation in an isotropic medium and $\epsilon(\omega)$ is the dielectric function.

It is noteworthy that the above integral function has a spatial distribution which peaks sharply very close to the specularly reflected beam direction. The angular width of this distribution has been deduced to be approximately $\hbar\omega/2E_0$, where $\hbar\omega$ and E_0 are the phonon and electron energy, respectively [6]. As E_0 is increased the distribution width is diminished and, accordingly, the analyzer samples a larger fraction of the distribution. Consequently, for emission of a surface optical phonon, the scattering probability integrated over the total solid angle and normalized to that of the specular beam can be computed without loss of accuracy. This integration yields $\Gamma=KE_0^{-1/2}$, where K is a constant.

It has been shown both theoretically and experimentally [6,11] that the total probability (Γ_N) for an electron to excite N quanta as it passes by a surface, with a corresponding energy loss of $n\hbar\omega$, can be characterized by a Poisson distribution $\Gamma_N=(\Gamma^N/N!)\exp(-\Gamma)$. It follows from the Poisson distribution that the intensity of the Nth multiple loss decreases by a factor of Γ/N ($\Gamma<1$) relative to that of the $(N-1)$th loss. This relationship, together with the above characteristic energy dependence of $E_0^{-1/2}$, suggests the use of an electron beam with a high impact energy to decrease the intensities of multiple phonon losses in HREEL spectra. Figure 1 demonstrates how the multiple losses diminish with increasing impact energy, E_0. Figure 2(a) shows plots, which closely approximate Poisson distributions, of the multiple losses due to excitation of N quanta of the MgO surface phonon at

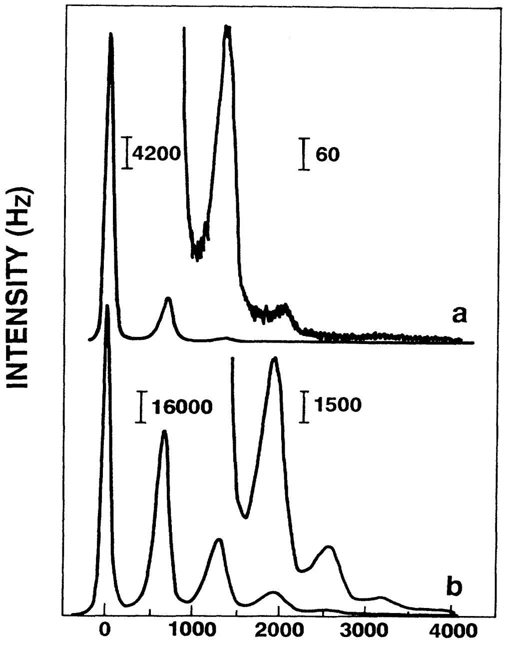

FIG. 1. HREELS spectra acquired from a ~30-ML MgO(100) film on Mo(100) with primary energies of (a) 46.2 eV and (b) 3.2 eV, respectively. The electron beam was incident at 60° with respect to the surface normal. The spectra were collected in the specular direction and at 90 K. The vertical scales represent electron counts.

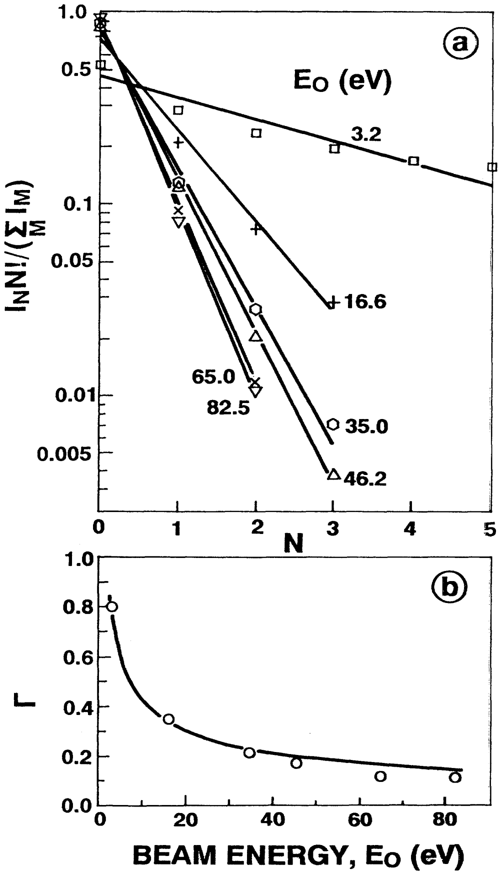

FIG. 2. (a) Poisson distribution of multiple losses due to excitation of N quanta of the MgO surface phonon at various primary energies indicated. (b) The scattering probability Γ corresponding to excitation of the fundamental mode of the MgO surface phonon as a function of E_0.

various impact energies. With the exception of $E_0=3.2$ eV, where the experimental points exhibit a deviation from the theoretically predicted straight line, the overall agreement between our experiment and theory is excellent. In Fig. 2(b), the scattering probability Γ is plotted as a function of E_0. The experimental points, obtained from the slope of each line in Fig. 2(a), agree excellently with the energy dependence of $E_0^{-1/2}$ [the solid curve in Fig. 2(b)].

It is known that the Fuchs-Kliewer surface optical phonon has a small wave-vector component parallel to the surface and has a long characteristic penetration depth [5,6]. It is therefore possible to further decrease the phonon-loss peaks by acquiring the spectra in an off-specular scattering geometry, i.e., in the impact-scattering regime. The further diminution in intensity of the phonon losses is indeed observed in our experiments which follow.

Figures 3(a)-3(d) give a set of HREELS spectra of H_2O adsorbed on a ~30-monolayer (ML) MgO film at 90 K as a function of annealing temperature (T). Water exposures were performed via backfilling the UHV chamber. Exposing the sample to 100 langmuir (L) (1 $L=1\times10^{-6}$ torrs) H_2O leads to the appearance of two distinct peaks in the spectrum [Fig. 3(a)]. The losses at 1650 and 3369 cm^{-1} are attributed to the excitations of the δ(HOH) scissor and ν(OH) stretching modes, respectively [12]. The δ(HOH) scissor mode was not well resolved in the specular spectrum even with a high-impact-energy beam because of its superposition with the second phonon loss. It is noteworthy that the 3369-cm^{-1} peak is considerably broadened due to hydrogen bonding [12], indicating that multilayers of water are condensed on the surface. Upon annealing to $T>160$ K, the ν(OH) feature shifts to higher loss energies [Fig. 3(b)]; concurrently our temperature-programmed desorption (TPD) spectrum indicates desorption of the H_2O multilayers [13]. Since infrared spectroscopic studies have shown that the absorption bands of the surface hydroxyl groups of MgO range from 3600 to 3770 cm^{-1} [14], the peak at 2988 cm^{-1} is inconsistent with a surface hydroxyl and possibly is due to a trace contaminate during the exposure of water. As T is increased, however, only the ν(OH) loss feature remains. This peak becomes sharper and finally disappears at $T>600$ K. A similar behavior was observed for the adsorption of D_2O. Figure 3(f) shows the spectrum of adsorbed D_2O following an anneal to 180 K, where the ν(OD) feature is shifted to a higher loss energy relative to that (at 2500 cm^{-1}) obtained from D_2O multilayers.

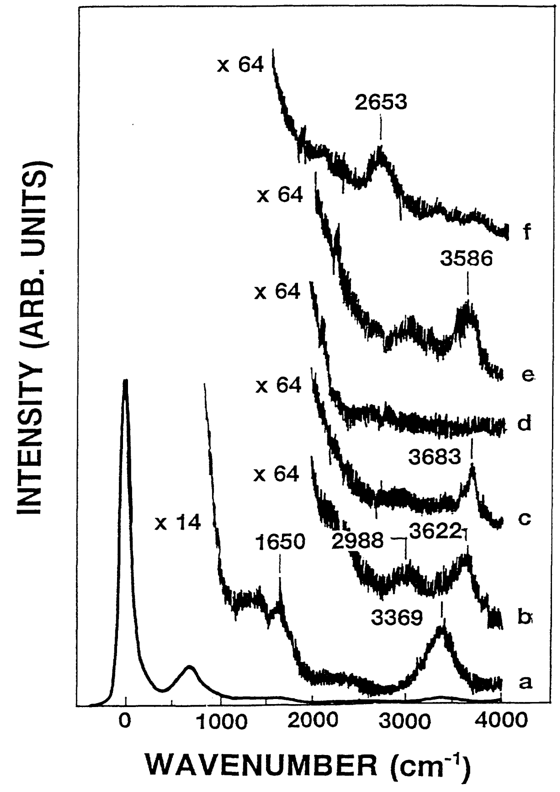

FIG. 3. HREELS spectra of water adsorbed on a ~30-ML MgO film at 90 K. (a) 100 L H_2O at 90 K; (b) 100 L H_2O, flash to 215 K; (c) 100 L H_2O, flash to 250 K; (d) 100 L H_2O, flash to 900 K; (e) 1 L H_2O at 90 K; (f) 100 L D_2O, flash to 180 K. 1 langmuir (L) $=1\times10^{-6}$ torrs. The spectra were collected at $E_0\simeq46$ eV and an angle 8.5° off the specularly reflected beam direction.

The shift of the 3369-cm^{-1} peak can be explained to arise from the desorption of the condensed H_2O multilayers and the subsequent dissociation of chemisorbed H_2O [15]. Regarding this point, it is noteworthy that the H_2O dissociation on metal surfaces usually results in an upward shift in ν(OH) frequency [12].

Dissociative adsorption of H_2O at low exposures occurs even at 90 K, as shown in Fig. 3(e). The 3586-cm^{-1} peak arising from H abstraction is nearly identical to the one observed in the annealing experiments. The same behavior was observed for isotopic water adsorption. Previous photoemission studies [16] have shown that water dissociates to form hydroxide anions on the (100) and (111) faces of single-crystal MgO at 298 K. The dissociative adsorption of water on NiO(111)/Ni(100) [17] and on oxidized Al(111) [18] has also been reported using HREELS.

Adsorption of methanol on thin MgO(100) films has also been examined using HREELS, as shown in Fig. 4. Exposing the specimen to 180 L CH_3OH produces four distinct peaks at 1143, 1437, 2947, and 3302 cm^{-1}. These losses can be attributed to C-O stretching [ν(CO)], CH_3 bending [$\delta(CH_3)$], C-H stretching [ν(CH)], and O-H stretching [ν(OH)] modes, respectively [9]. These loss features were essentially preserved throughout the 90-145-K annealing temperature range; however, spectra acquired using a low-energy beam ($E_0=3.2$ eV), following an anneal to 145 K, were indistinguishable from the spectrum of the clean surface. The

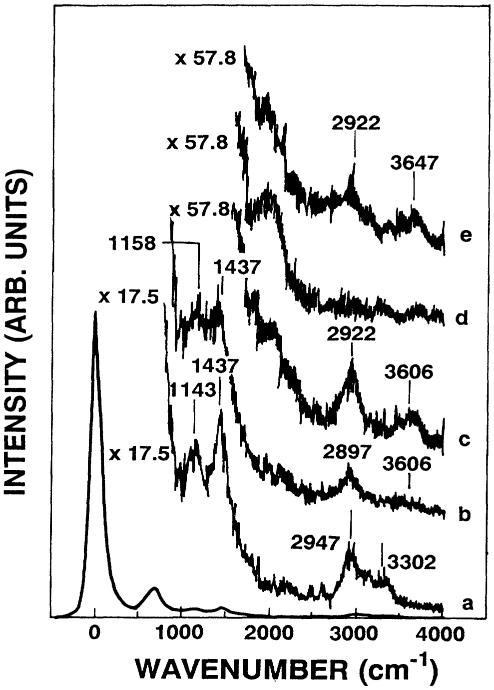

FIG. 4. HREELS spectra of methanol adsorbed on a ~30-ML MgO film at 90 K. (a) 180 L CH_3OH at 90 K; (b) 180 L CH_3OH, flash to 160 K; (c) 180 L CH_3OH, flash to 273 K; (d) 180 L CH_3OH, flash to 490 K; (e) 5 L CH_3OH at 90 K. The spectra were collected at $E_0 \approx 46$ eV and at an angle 8.5° off the sepcularly reflected beam direction.

spectrum of Fig. 2(b), acquired following an anneal to 160 K, exhibits loss features of the methanol monolayer; the desorption of methanol multilayers occurs in the 137–166-K range with a maximum at 146 K, as indicated by our TPD measurements. The method outlined here then does facilitate the direct observation of the relatively weak adsorbate losses over a wide spectral range (in this case, 1000–4000 cm^{-1}) without serious interference from multiple phonon losses.

Annealing to $T \geq 160$ K resulted in the disappearance of the 3302-cm^{-1} loss, and the appearance of a new peak at 3606 cm^{-1}. The 2947-cm^{-1} loss feature remained unperturbed. The appearance of the new feature at 3606 cm^{-1}, identical to the one assigned to OH species, indicates dissociation of methanol and the formation of methoxy upon annealing. However, increasing the annealing temperature results in the concurrent diminution of the two losses. The loss feature finally disappears at $T = 490$ K, as indicated in Fig. 4(c). The dissociative adsorption of methanol at 90 K was also observed at low exposures, as shown in Fig. 4(d).

In conclusion, a new approach to the application of HREELS to adsorbates on ionic substrates has been demonstrated in this Letter. Of special significance is that this technique facilitates the direct measurement of relatively weak vibrational loss features of adsorbates on an insulating surface, thereby allowing a comparison to analogous infrared studies. These latter studies have been extensively used in the investigation of high-surface-area catalysts which often consist of polar materials.

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