Resonance Scattering of Electrons from N_2, CO, O_2, and H_2 Adsorbed on a Silver Surface

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Inelastic electron scattering from the vibrations of N_2, CO, O_2, and H_2 adsorbed in monolayers and multiple layers on Ag films at $T \sim 20$ K show energy-dependent cross sections characteristic of resonance scattering via temporary negative-ion states. The resonances for these adsorbed phases generally occur at lower energies than in the gas phase and have spectral features which indicate negative-ion lifetimes of less than 10^{-14} sec.

We present the first electron scattering study which demonstrates the occurrence of short-range resonance scattering from molecules adsorbed or condensed on a metal surface. Our measurements of the energy-dependent scattering cross sections for the excitation of fundamental and overtone vibrations of N_2, CO, O_2, and H_2 adsorbed molecularly at ~20 K onto poly-crystalline Ag films show resonance structure analogous to that occurring in the gas phase. From the features of these molecular resonances, we obtain new insight as to the physics of temporary negative-ion states and resonance electron scattering in these adsorbed phases.

The observation and identification of such resonance electron scattering from adsorbates on surfaces has not been possible in previous studies,[1-5] partly because of diffraction effects associated with the use of single-crystal substrates.[6] Resonance scattering from adsorbed species is important to understand as it (a) can dominate impact scattering and sometimes even dipole scattering,[7,8] (b) provides an excitation mechanism to observe higher vibrational modes, and (c) may provide independent information to derive adsorbate orientation and structure.[9]

The experimental apparatus consists of an ion- and sublimation-pumped UHV chamber which contains a cryogenic sample holder, an ion-sputter gun, a Ag evaporation source, and an energy-loss spectrometer. This spectrometer utilizes hemispherical deflectors as energy-dispersing elements ($E_{pass} = 0.5$ eV) and has the analyzer and monochromator at a fixed scattering angle of 90°. Other characteristics are described elsewhere.[10] In order to measure energy-dependent cross sections, the loss spectra were taken at a variety of beam energies whose absolute values were determined from the cutoff in each loss spectra. We use the elastic intensity to normalize our loss intensities so as to obtain relative

scattering cross sections. This procedure does not significantly alter the shape or position of the resonance since the elastic scattering cross sections show only a weak energy dependence.

The sample holder consists of a copper block which was cooled by an Airco cryotip to 20 K as measured with a carbon resistor. The copper block could not be rotated and was oriented ~3° from specular scattering conditions ($\theta_i = 42°$, $\theta_0 = 48°$). Ag was evaporated from a Ta boat source onto the cooled copper block to yield polycrystalline films. The elastic scattering intensities from our films were comparable to the off-specular elastic scattering found in earlier studies of Ag(111).[10]

The adsorbates were exposed to the sample for prescribed dosages (given in Langmuirs, 1 L $= 10^{-6}$ Torr sec) where we have applied the appropriate ion-gauge correction factors. We finally note that once at cryogenic temperatures, the system pressure dropped from its typical working value of 8×10^{-11} to ~3×10^{-11} Torr. Some adsorption of background residuals also occurred on our sample, but were kept to a minimum by short (~15 min) measurement times.

As a representative sample of our raw data, we show in Fig. 1 the energy-loss spectra for a 1-L exposure of Ag to N_2 for two incident beam energies, E_B. These two spectra are part of a sequence of spectra for E_B between 0.5 to 4 eV from which we derive relative scattering cross sections. In the 4-eV spectrum we observe the fundamental vibration of molecular N_2 at 295 meV which closely corresponds to its gas-phase value of 292 meV.[11] For $E_B = 1.5$ eV, however, we observe strongly enhanced inelastic scattering from both the fundamental and overtone vibrations of N_2. Such behavior is characteristic of resonance electron scattering as will be discussed later. The extra loss peaks at 195 and 460 meV become observable only at higher energies. We
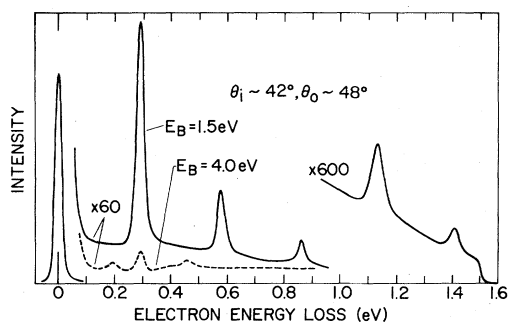
FIG. 1. Electron energy loss spectra for one mono-layer of N_2 adsorbed at 20 K onto silver for incident beam energies of 1.5 and 4 eV. The spectrum which is off resonance for N_2 (dashed curve) is slightly down-shifted and shows trace contamination (~ 0.02 mono-layers) of O_2 and H_2O (possibly OH) species. The scale magnifications in the loss region are indicated.

attribute these losses to ~0.02 monolayers of O_2, H_2O, and possibly OH contaminants which have resonances at higher energies than N_2.[7,8] All adsorbates studied here show fundamental vibra-tional frequencies within 5 meV of their gas-phase values and reversibly desorb above $T \sim 70$ K, indicative of weak adsorption.

In Fig. 2 we summarize the energy-dependent inelastic scattering cross sections characteristic of monolayer (solid lines) and condensed (dashed lines) N_2, CO, O_2, and H_2 on Ag at 20 K. For comparison the corresponding gas-phase cross sections are also shown (dotted lines). For clar-ity we show only the cross sections for the $v = 0$ $\rightarrow v = 1$ vibrational excitations, except for CO, where we show $v = 0 \rightarrow v = 2$ to avoid its stronger dipole scattering distributions. The difference in the excitation spectra of the adsorbed and con-densed phases of N_2 and CO allow us to detect the formation of the first condensed layer and thus delineate the monolayer and multilayer re-gimes. However, we have not observed signifi-cant coverage-dependent changes in the excita-tion profile near monolayer coverages (i.e., $0.5 \le \theta \le 1$). For O_2 and H_2, additional features occur in the electronic and vibrational loss spec-tra, respectively, which further allow us to delineate these regimes (but are not discussed here). In all cases these regimes are consistent with the exposure values.

The energy-dependent cross sections shown in Fig. 2 cannot be explained by dipole scattering theory alone and for free molecules are attributed to resonance scattering associated with the for-mation of a temporary negative-ion state in the
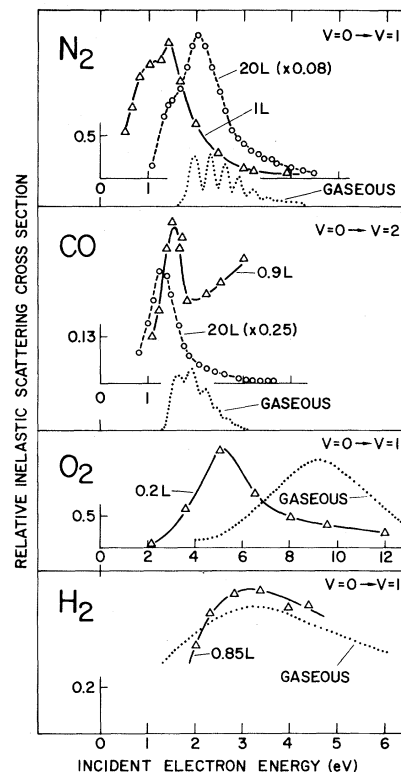

FIG. 2. Relative inelastic scattering cross sections for N_2, CO, O_2, and H_2 adsorbed on silver (solid lines). The dashed lines represent condensed multilayers of N_2 and CO while the dotted lines are the gas-phase spectra (N_2, CO, and O_2 from Ref. 8 and H_2 from Ref. 12). The ordinate values shown are percentage in-tensities relative to the elastic beam.

molecule.[7,8] In the gas phase these correspond to the $\tilde{X}\,^2\Pi_g$, $\tilde{X}\,^2\Pi$, and $\tilde{X}\,^2\Sigma_u{}^+$ negative-ion states of N_2, CO, and H_2, respectively,[7,8] and the $^4\Sigma_u{}^-$ or $^2\Pi_u$ ion states of O_2.[13,14] The presence of these energy-dependent structures in our inelastic scat-tering cross sections, the correspondence to the known gas-phase resonances, as well as the aforementioned excitation of higher overtones, all indicate molecule-derived resonance scatter-ing from these adsorbed molecules.

The generally observed reduction in the reso-nance energy from that observed in the gas phase offers further support for the involvement of a charged intermediate state, i.e., a negative ion. The attractive interaction between the negative ion and its image in the metal,[15] or the polariza-tion of the surrounding condensate, will reduce the potential energy of the ion state. This will shift the resonance to lower energies as observed. Similar screening effects are well known to occur

for the photoionization of adsorbed and condensed molecules on surfaces.[16]

For N_2 and CO we also observe the disappearance of the modulations in the gas-phase resonances (see Fig. 2). These modulations arise from an interference of the outgoing nuclear wave packet with its reflection from the classical turning point and occur for negative-ion lifetimes of $\sim 10^{-14}$ sec.[7,8,17] For negative-ion lifetimes of $\sim 10^{-14}$ sec or longer, shifts and shape changes in the excitation profile occur for different overtones.[8,17] For shorter lifetimes, referred to as the impulse limit,[7,8,18] this interference structure does not occur and the scattering cross section has nearly the same energy dependence for each overtone.[18] We observe similar excitation profiles for the overtones of monolayer or condensed CO and N_2 (up to $v = 0 \rightarrow v = 7$ for condensed nitrogen). The disappearance of the interference structure in the N_2 and CO excitation profiles, the similarity of the excitation spectra of the different overtones, and the large widths of these profiles, all indicate that resonance scattering from adsorbed and condensed CO and N_2 occurs in the impulse limit. The reduced autoionization lifetime for adsorbed phases is reasonable since the symmetry which provides the centrifugal barrier for the electron in the gas phase is now broken.[19] Although a detailed analysis is necessary to determine precise lifetimes,[18] our observed widths suggest lifetimes in the $10^{-16} - 10^{-15}$-sec range for adsorbed (or condensed) N_2, CO, and O_2. The broad profile for H_2 is even more complicated to analyze because of possible nonresonant scattering contributions.[19]

We also comment briefly on other features of our results which tend to be molecule specific. Remnants of the monolayer resonances of CO and N_2 occur in the multilayer spectra and, for example, produce the low-energy shoulder in condensed N_2 (see Fig. 2). For monolayer N_2 another low-energy shoulder is reproducibly observed which we speculate may arise from two different bonding sites or orientations on our polycrystalline film. Also for CO the monolayer resonance occurs at a higher energy than the condensed-phase resonance — a fact we tentatively attribute to (repulsive) dipole-dipole interactions associated with oriented CO in the monolayer regime. In the case of O_2 the strong shift in resonance energy may reflect a specific interaction of O_2^- with the surface which may also be related to the shape change in its resonance profile. Finally, although the absence of a shift in the resonance of ad-

sorbed H_2 to lower energies may be obscured by its breadth, the lack of a shift offers further support for nonresonant scattering contributions for H_2.[20] The reduced symmetry at the surface may also enhance such nonresonant scattering.

In conclusion, we have observed resonance electron scattering via temporary negative-ion states for N_2, CO, O_2, and possibly H_2 adsorbed or condensed on Ag at 20 K. The energies of these molecular resonances are generally reduced on the surface or in the condensed phase relative to the gas phase. The lifetimes of the temporary negative-ion states of CO and N_2 are decreased by about an order of magnitude, and all molecules studied show features characteristic of the impulse limit, i.e., lifetimes less than 10^{-14} sec. Although our study deals with weak-adsorption systems, we expect that the corresponding negative-ion states of more strongly interacting adsorbate-substrate systems will have even shorter lifetimes associated with greater distortions in the centrifugal barrier. This may, in part, account for previous difficulties in observing such resonances.

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Rotational Energy Transfer in Direct Inelastic Surface Scattering: NO on Ag(111)

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Rotational state distributions for NO scattered from Ag(111) have been measured over the incident kinetic energy range of 0.1 to 1.7 eV with use of rotationally cold molecular beam and laser-induced–fluorescence detection. The measured distributions divide into two parts: a low rotational state portion ($J \lesssim 20.5$) which is described by a Boltzmann distribution and a high-J portion which shows a broad structure tentatively interpreted as resulting from a rotational rainbow.

The understanding of trapping and sticking of atoms and molecules at surfaces requires an understanding of the various energy-loss mechanisms involved in collisions with surfaces. For atoms, momentum distribution measurements of scattered particles are providing much insight into the underlying dynamics; for molecules, however, measurements of internal-energy distributions are also required. Rotational energy transfer is of particular interest because both experiment[1] and theory[2] provide indirect evidence for a facile interchange of translational and rotational energy in molecular scattering.

Recently there has been considerable interest in the direct measurement of rotational state distributions for surface-scattered molecules by laser-induced–fluorescence (LIF) detection. Using LIF detection, one can determine molecular internal-state distributions by tuning a laser through an adsorption band of the molecule and measuring total fluorescence to provide a very sensitive measure of the adsorption spectrum. Using this technique, Frenkel *et al.*[3] observed a 280-K Boltzmann rotational distribution for a rotationally cold beam of NO scattered from (NO-covered) Pt(111) at 290 K and conclude that this results from trapping and complete accommodation followed by desorption. Measurements from a carbon-covered Pt(111) surface[3] showed small departures from a Boltzmann distribution for low rotational states. McClelland *et al.*[4] reported that making a 300-K thermal beam of NO collide with an Ag(111) surface results in a Boltzmann

rotational state distribution for the scattered particles with partial accommodation to the surface temperature. They were unable, however, to determine if this results from direct scattering or from trapping followed by desorption. Partial rotational accommodation has also been observed for CO scattered from LiF.[5]

To distinguish and characterize the various energy-transfer channels involved in atom-surface scattering, it has proven extremely useful to measure scattered-particle energy distributions as a function of surface temperature, incident energy, and incident and final angle.[6] For molecular scattering, such measurements are needed not only of the translational energy distributions, but for internal-energy distributions as well. We report here LIF measurements of internal-energy distributions of a rotationally cold beam of NO molecules scattered from an Ag(111) surface. The dependence on incident kinetic energy, E_i, and incident angle, θ_i, has been measured for the first time as have angular and velocity distributions for molecules scattered in specific rotational states, J. Measurements carried out for higher J than previously reported[3,4] reveal interesting new phenomena; sharp departures from a Boltzmann distribution are observed for the higher incident energies. The results support a direct scattering mechanism for the range of conditions studied here and show the inadequacy of the physical picture of partial accommodation to the surface temperature suggested in earlier work.

The experiment is based on measuring the la-