Physisorption of CO and N_2 on Al(111): Observation of surface-molecule vibrations in electron resonance scattering

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Monolayers of physisorbed CO and N_2 on Al(111) were investigated by means of high-resolution electron-energy-loss spectroscopy (HREELS). The line shapes of the $v=0\rightarrow1$ molecular stretching modes differ largely. In the high-energy-loss tail of this mode, surface-molecule stretching losses are detected with an energy of 10.5 meV in the case of N_2. It is demonstrated that this large inelastic intensity is due to the negative-ion resonance scattering mode operating for N_2 but not for CO. The results are discussed in the framework of Gadzuk's wave-packet method for time-dependent quantum behavior of molecules on surfaces.

Molecular dynamics on surfaces is a recent and very challenging topic in surface science. It is closely connected to internal state excitation in molecular-beam scattering and stimulated desorption phenomena. The observation of vibrational overtone losses in resonance high-resolution electron-energy-loss spectroscopy (HREELS) is not so often mentioned in this context. In some HREELS studies of molecules physisorbed on surfaces, greatly enhanced overtone excitation of intramolecular modes of the diatomic molecule have been found.[1-3] By comparison with gas-phase data, these excitations have been understood as due to temporary negative-ion resonances. The cross section appeared as a smoothed gas-phase version shifted down in primary energy by ~1.0 eV through the image potential at the surface.

More recently, Gadzuk[4,5] has discussed a semiclassical model of this scattering process and has pointed to the molecular dynamical aspect of this phenomenon. He explicitly expected "that (low-frequency) surface-molecular modes should show an enhancement in excitation probability as the primary electron energy is tuned through a negative-ion shape resonance associated with the high-frequency intramolecular stretch mode" of a diatomic molecule. This is exactly what we have observed experimentally.

Recently, we have investigated physisorbed layers of CO and N_2 on Al(111) at 20 K.[6] By an *in situ* combination of HREELS and uv photoelectron spectroscopy, we have clearly differentiated between monolayers and multilayers of physisorbed CO and N_2. By varying the primary energy of the incoming electrons and the exit angle of the outgoing electrons, we have been able to demonstrate that for excitation of the first molecular stretching vibrations, the dipole scattering mode operates for CO and the resonance scattering mode for N_2 at a primary energy of 1.5 eV.

Here we report on the differences in line shape for the $v=0\rightarrow1$ stretching mode of CO and N_2 physisorbed in a monolayer (ML) on Al(111). Compared to the known work,[1-3] we have increased the energy resolution by a factor of 4 so that we have been able to observe the surface-molecule vibrations of a physisorbed species (N_2)

for the first time. This provides an important contribution for the evaluation of potential-energy curves for weakly bound species. Furthermore, comparing CO and N_2, we can conclude that the difference in line shape is caused by the difference in scattering mechanism in line with Gadzuk's model.

Our paper is organized as follows: After a brief summary of the experimental arrangement, we present our results which are then discussed by adopting the semiclassical approach of Gadzuk. The experiments were performed in an UHV system with a base pressure of 3×10^{-11} mbar. The electron-energy-loss spectrometer is of the hemispherical deflector type[7] and is operated at an energy resolution of less than 10 meV. The primary energy of the electrons was 1.5 eV in order to maximize the scattering cross section. A He discharge lamp is also mounted on the same spectrometer in order that ultraviolet photoemission spectroscopy (UPS) may be performed under conditions identical to those of HREELS. The Al(111) sample was cooled to about 20 K by liquid He. Before each experiment the sample was cleaned by Ar ion bombardment for three hours and annealing at 770 K for 10 min. N_2 and CO were dosed via different UHV dosing lines. The purity of N_2 was 99.9999% and that of CO, 99.997%. Special care was taken to keep the H_2O background pressure as low as possible in order to avoid H_2O coadsorption during the measurements when the sample was cooled to 20 K.

In Fig. 1 typical HREELS spectra are shown for the clean Al(111) surface and for the ML of physisorbed N_2 and CO. The clean surface exhibits a smooth background without any indication of other losses than the 32-meV loss which is so far unobserved and which we attribute to a surface phonon without further discussion here. The ML of CO is characterized by a single loss at 265 meV (2137 cm^{-1}) which was assigned to the CO stretching mode since its energy is very near to the gas-phase value of 266 meV.[8] Also for the N_2 layer only one loss at 290 meV (2339 cm^{-1}) is found near the gas-phase value of 289 meV.[8]

We have discussed these results recently with respect to the orientation of the CO molecule.[6] Here we concen-
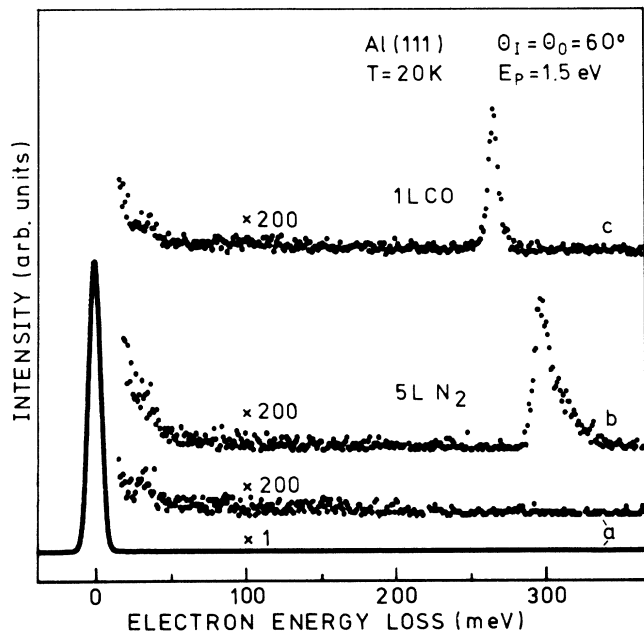
FIG. 1. HREELS spectra for (a) the clean Al(111) surface, (b) a N_2 monolayer, and (c) a CO monolayer. The sample temperature during and adsorption measurements was 20 K. The angle of the incoming (θ_I) and outgoing (θ_O) electrons and the energy E_p of the incoming electrons are given. The gas doses are given in units of langmuirs [1 langmuir $(L) \equiv 1 \times 10^{-6}$ Torr s].

trate on the striking differences in line shape. Whereas CO exhibits very much the same line shape as the primary beam, N_2 possesses a wide tail to higher energies. The $v=0 \rightarrow 1$ line is shown with a better signal-to-noise ratio in Fig. 2. We have performed a curve fitting into Gaussians taking the half-width in energy from the no-loss edge of the main line (on the left side in Fig. 2). The fit using five lines reproduces the experimental result quite accurately. From the energy distance between the
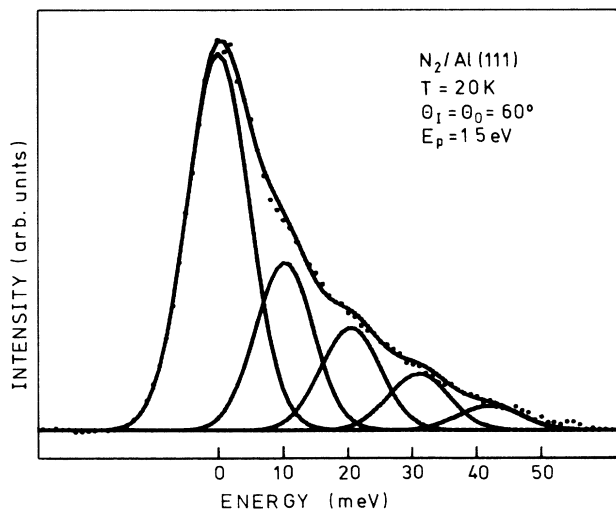

FIG. 2. HREELS spectrum of the $v=0 \rightarrow 1$ stretching loss of the N_2 monolayer. The parameters are the same as for Fig. 1. The dots are for the measurements. The lines are for the single loss curves and the sum curve.

different losses of 10.5 meV, we interpret these losses as due to the surface-molecule vibrations. For a chemisorbed CO or N_2 molecule these vibrations are known to have an energy of about 50 meV. Estimating the potential depth for the physisorbed N_2 molecule to be in the order of 100 meV, an energy of about 10 meV for a surface-molecule vibration seems quite reasonable for the physisorbed monolayer species. If we denote the molecular stretching vibrations by v and the surface-molecule vibration by $\bar{v}$, the lines of Fig. 2 may be assigned with increasing loss energy as follows: $v=0 \rightarrow 1$, $\bar{v}=0 \rightarrow 0$ (1.00); $v=0 \rightarrow 1$, $\bar{v}=0 \rightarrow 1$ (0.43); $v=0 \rightarrow 1$, $\bar{v}=0 \rightarrow 2$ (0.27); $v=0 \rightarrow 1$, $\bar{v}=0 \rightarrow 3$ (0.15); $v=0 \rightarrow 1$, $\bar{v}=0 \rightarrow 4$ (0.068). The values in parentheses stand for the relative intensities.

Starting the discussion of the results, we stress that the scattering mode for excitation of the $v=0 \rightarrow 1$ molecular stretching vibration is the dipole mode for CO and the impact mode for N_2.[6] Therefore, the difference in line shapes is quite obviously caused by the difference in scattering modes. For the dipole scattering mode it is well known that the excitation, e.g., of overtones for the stretching mode, is very small,[9] whereas it is high for the impact mode as observed for physisorbed diatomic molecules.[1-3] This behavior, observed so far for the molecular stretching mode, is found here for the surface-molecule vibrational mode for the first time. Comparing the energy of this loss of 10.5 meV with our energy resolution, one realizes that we are just at the limit of our capability to observe this loss but we are not able to resolve any variation of energy between the different overtones. Any asymmetry of the potential-energy curve is known to give rise to the inequivalence $E_{\bar{v}} < \bar{v}E_1$.

In order to explain the strong overtone intensities of the surface-molecule stretching mode connected with the excitation of the $v=0 \rightarrow 1$ molecular stretching mode, we use Gadzuk's model.[5] He has adapted the wave-packet method, for the description of time-dependent quantum behavior in molecular systems, to surface problems. In Fig. 3 potential-energy curves are sketched as a function of distance z normal to the surface. The curves in the upper part of Fig. 3 are for time $t=0$ when the incoming electron gets trapped into the negative-ion resonance; the curves in the lower part are for the time $t=\tau_R$ when this electron leaves the molecule. The negative-ion resonance is described in this model by a transition between the N_2^- and N_2 potential-energy curves. The N_2 curve describes the N_2 surface interaction and is characterized by an equilibrium distance z_0 and some curvature from which the vibration frequency can be derived. At $t=0$ the incoming electron is trapped into the negative-ion resonance state depicted in the upper N_2^- curve. The negative charge induces a positive (screening) charge within the substrate. The interaction between the captured electron and its image provides an additional, attractive term augmenting the neutral potential energy. The new equilibrium distance is $z_0^+ < z_0$ and also the curvature is expected to be different as indicated in the upper potential-energy curve in Fig. 3 for $t=0$.

With some simplifications[5] it is possible to separate the molecule-surface interaction into "slow" and "fast"
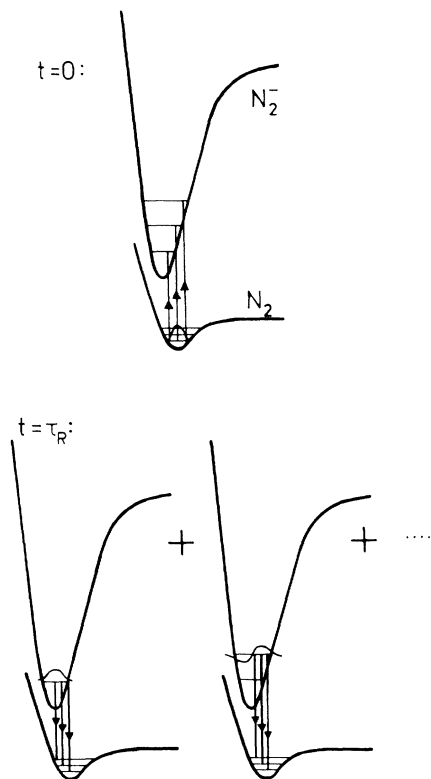
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FIG. 3. Potential-energy curves describing the interaction between physisorbed molecules and the surface for N_2 and N_2^-. Transitions into the N_2^- state at $t=0$ and back into the ground state at $t=\tau_R$ are indicated by arrows.

parts. The slow parts consist of transitions including nuclear motions as translation, vibration, and rotation. Potential-energy curves for the translational degree of freedom normal to the surface are depicted in Fig. 3. The fast parts consist of electronic transitions and may be described as transitions between potential-energy curves of a slow part that allows for motion and redistribution of energy among the various slow degrees of freedom.

During the life time τ_R ($\sim 10^{-15}$ s) of the negative molecular ion, the excited system is described as a wave packet moving along a classical trajectory. At $t=\tau_R$ the wave packet, which is time evolved on the final-state potential-energy surface, is projected back onto the initial-state potential-energy surface. Due to the changes, introduced during propagating in the final state, a Franck-Condon overlap with higher vibrational modes in the initial state occurs. This is indicated in the lower part of Fig. 3, i.e., at $t=\tau_R$ where only the first two terms of the Fourier sum of the negative-ion state are sketched.

It should also be noted that the same kind of model was used by Gadzuk to explain the high probability of overtone excitation of the molecular vibrational mode as observed in the experiment.[4] We discuss here the surface-molecule vibrational overtones connected with the $v=0\rightarrow 1$ transitions since it is experimentally the most simple case. They can be observed also for $v=0\rightarrow 0$, i.e., in the tail of the elastic peak and also with ($v=0\rightarrow n$, $n\geq 2$) modes. Actually, it can be seen in curve b of Fig. 1; however, two effects obscure or can ob-

scure the wanted overtone intensity: the foot of the elastic peak and also the difficult discrimination against librational modes of spurious amounts of H_2O which are found at these energies.

The surface-molecule vibrational mode is identified here for physisorbed N_2 whereas it is not observed for CO. The missing observability in case of CO is an interesting question of its own which will be addressed in future work. It probably indicates that the CO^- lifetime in the ML is too short to lead to significant excitation of such a mode. This is in accordance with gas-phase data for which it is known that the lifetime of CO^- is shorter than that of N_2^-.[10] On the other hand, we believe that the effect observed for N_2 is not of limited applicability since, e.g., some inelastic tails have also been observed recently for O_2 on Pd(111).[11]

From the relative transition probabilities of the N_2 surface vibrations, the lifetime of the N_2^- state can be deduced. For a classical harmonic oscillator it is known that the probability P for excitation of a transition $0\rightarrow n$ is given by a Poisson distribution,

$$P_{0\Longrightarrow n}=e^{-\beta}(\beta^n/n!)\ ,$$

where the parameter β is given by the ratio between the overall gain in energy and the quantum energy of the individual transition. Our P values, which have been given above, do not fit to a Poisson distribution. Gadzuk[5] has pointed out that for a model as sketched in Fig. 3 for which the force constants (curvatures) are different for the excited and the ground state, a Poisson distribution is not expected in agreement with our experiment. Also, it should be noted that we should summarize the $\tilde{v}=0\rightarrow m$ transitions over all $v=0\rightarrow n$ transitions to get the complete intensity distribution.

Nevertheless, we can deduce approximate values of β from $P_{0\Longrightarrow 0},P_{0\Longrightarrow 1}/P_{0\Longrightarrow 0}$ or $P_{0\Longrightarrow 2}/P_{0\Longrightarrow 0}$. Gadzuk[5] has derived a formula for which the lifetime τ_R is connected with β and the N_2^- potential. Using this formula, we have calculated $\tau_R=5.5\times 10^{-15}$ s (4.5×10^{-15} s; 5.9×10^{-15} s) from $\beta=0.64$ (0.43; 0.73).

In conclusion, we have observed the surface-molecule vibrational mode of a monolayer of physisorbed N_2 on Al(111). This loss and its overtones are found in the high-energy-loss tail of the $v=0\rightarrow 1$ molecular stretching mode in HREELS with the primary energy tuned to the negative-ion resonance of N_2 at 1.5 eV. Since these losses are not found for the $v=0\rightarrow 1$ transition of the physisorbed CO ML and since for this species the scattering mode is dipole active, we have demonstrated that the high cross section for excitation of overtones of the surface-molecule vibration is caused by the negative-ion resonance scattering. Some qualitative arguments have been given to understand this phenomenon in terms of a wave-packet method adopted by Gadzuk to time-dependent quantum behavior of molecules at surfaces. Our findings open up a new possibility of contributing to the evaluation of the potential-energy curves for physisorbed molecules at surfaces.

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