

## Vibrational structure in the $N_2^-$ ( ${}^2\Pi_g$ ) electron resonance of $N_2$ films

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The formation of a temporary  $N_2^-$  state around 2 eV in electron scattering from  $N_2$ -covered metal surfaces is established by resolving the vibrational structure of the anion in the  $\nu = 1, 2, 3,$  and 4 decay channels of ground state  $N_2$  and by the demonstration of the presence of a "boomerang" effect. The average vibrational energy (0.29 meV) and the lifetime ( $\sim 3 \times 10^{-15}$  sec), which are close to the gas-phase values, indicate that the solid-phase anion has a symmetry similar to the  ${}^2\Pi_g$  configuration.

Recent electron-energy-loss measurements of vibrational excitation of adsorbates have revealed the presence of electron resonances in monolayer and multilayer films of  $O_2$ ,  $N_2$ , and  $CO$  deposited on metal surfaces.<sup>1-3</sup> In  $N_2$  multilayer films,<sup>3</sup> the presence of four maxima in the vibrational excitation functions, corresponding to the four shape resonances of the  $N_2^-$  gas-phase system, strongly supports the hypothesis that enhancement of vibrational excitation in these films occurs via the temporary localization of a projectile electron in the vicinity of a single molecular site. The localized state would be a temporary negatively charged ion with a molecular configuration related to that of the corresponding gas-phase shape resonance.<sup>4</sup>

We report here measurement of oscillatory structure in the lowest-energy electron resonance in  $N_2$  films. These are the first data where the vibrational structure of a transient negative ion can be observed in the condensed phase. The *spectroscopic information* gained from this experiment allows us to estimate the lifetime, the relaxation shift, the average vibrational energy of the anion, and to demonstrate the presence of a "boomerang" effect. These results establish the formation of a transitory  $N_2^-$  state, with a symmetry closely related to the  ${}^2\Pi_g$  configuration, in electron scattering from solid multilayer  $N_2$  films between 1 and 3 eV. At monolayer and submonolayer coverage the state symmetry appears to be greatly perturbed by the metal surface.

Basically, the apparatus<sup>1</sup> consists of two concentric hemispherical electrostatic deflectors and a closed-cycle refrigerated cryostat. Both components are housed in an UHV system<sup>5</sup> reaching *working* pressures below  $5 \times 10^{-11}$  torr. Electrons leaving the monochromator are focused on a clean polycrystalline platinum ribbon secured by a press fitted to the cold end of the cryostat. This latter is mounted on an *xyz* manipulator. The angle of the incident beam can be varied from  $14^\circ$  to  $70^\circ$  from the normal. Condensed layers are grown on the ribbon and the film thickness

estimated, within 50% accuracy, as previously described.<sup>6</sup> Electrons reflected at  $45^\circ$  from the film are energy analyzed. The data were recorded with an overall resolution of 18 meV, a primary current of  $10^{-9}$  A and a cryostat temperature of 14 K. The film thickness was varied from submonolayer coverage to about 100 Å. The incident electron energy was calibrated within  $\pm 0.15$  eV with respect to the vacuum level by measuring the onset of electron transmission through the film.

Measurements of the excitation function between 0–30 eV for the first four vibrational levels of ground-state molecular nitrogen were recorded in multilayer  $N_2$  films and at submonolayer  $N_2$  coverage of the platinum substrate. The multilayer results showed the presence of four maxima in the excitation functions as previously observed<sup>3</sup> in the  $\nu = 1$  vibrational level at an incidence angle of  $14^\circ$ . The energies of the maxima were almost completely independent of the angle of incidence between  $14^\circ$  and  $70^\circ$  and their amplitude varied by less than a factor of 2 within these limits. These features were therefore not related to the film reflectivity whose structures varied considerably in energy and amplitude with the angle of incidence. An example is given in Fig. 1(a) for electrons incident at  $45^\circ$ , losing energy to the first vibrational level  $N_2$ , in an  $\sim 50$ -Å film. The four maxima were previously correlated<sup>3</sup> to the four shape resonances observed in the gas phase at 2.3, 8.0, 13.7, and 22 eV, respectively.<sup>4,7</sup>

The lowest-energy feature in Fig. 1(a) is displayed on an extended scale in Fig. 1(b) (i.e.,  $\nu = 1$ ) along with the energy dependence of the excitation function of the  $\nu = 2$  and  $\nu = 3$  vibrational levels of molecular nitrogen in the 0–5-eV region. The oscillatory structure, which modulates the broad peak in each excitation function, could only be clearly observed when the thickness of the film was greater than three monolayers. Its energy was independent of the angle of incidence between  $14^\circ$  and  $70^\circ$ . This structure is interpreted to result from vibrational

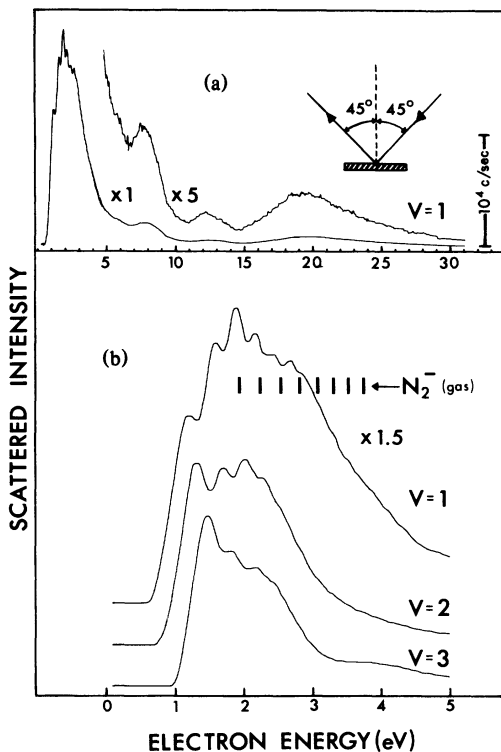


FIG. 1. (a) Energy dependence of vibrational excitation of the first vibrational level of ground-state  $N_2$  in  $\sim 50$ -Å multilayer molecular nitrogen film. The four maxima are interpreted as due to the formation of temporary  $N_2^-$  states in the region 0–30 eV. (b) Excitation function for the first three vibrational levels of  $N_2$  in the 0–5-eV region. The oscillatory structure is due to nuclear motion within the temporary  $N_2^-$  state.

motion of a transient  $N_2^-$  state. Similar features observed between 2 and 4 eV in gaseous  $N_2$  are ascribed<sup>4</sup> to vibrational motion of the  ${}^2\Pi_g$  state of  $N_2^-$ . The vertical bars in Fig. 1(b) represent the energies of the first eight “vibrational peaks” of that state as recorded<sup>8</sup> in the  $v=1$  decay channel. The average spacing between the first six of these vibrational peaks is 0.27 eV as compared to the corresponding value of 0.29 eV in the solid. From the shift of the first vibrational peak in the upper curve of Fig. 1(b) in going from 1.93 eV in the gas to 1.23 eV in the film, we find a value of 0.7 eV for the relaxation shift. At monolayer and submonolayer coverages, the relaxation energy is reduced owing to an increase in the average distance between  $N_2$  molecules and a decrease in their number around the negatively charged ion. This reduction tends to increase the energy of the  $N_2^-$  state but other phenomena can have an opposite effect. In particular, we expect the attractive potential between the anion and its image in the metal, and the possible lowering of the anion

symmetry by the metal, to reduce the resonance energy. Experimentally, we found that, at monolayer coverage, the first maximum in Fig. 1(a) is lowered by 0.6 eV with respect to the multilayer film value. A similar shift has been observed by Demuth *et al.*<sup>2</sup> for  $N_2$  adsorbed on a polycrystalline silver substrate. The vibrational structure seen in Fig. 1(b) was also observed in argon matrices containing 5 and 10 mol% molecular nitrogen and in  $N_2$  multilayer films covered by several (3 to 10) argon monolayers. These results clearly indicate that resonance electrons are not necessarily produced at the surface of a film but can emanate from the bulk of a solid. From the matrix experiments, we can further conclude that it is possible for an electron forming a resonance *in a solid* to be truly localized on a single molecular site during the lifetime of the compound state.

If the lifetime of the anion was long compared to a vibrational period of a  $N_2$  molecule, the oscillatory structure in Fig. 1(b) would form non-overlapping, well-defined peaks which would correspond to vibrational levels of an  $N_2^-$  state. On the other hand, if the lifetime was much shorter than a vibrational period, no structure would be observed. In the intermediate case (i.e., lifetime of the order of the vibrational period) overlapping oscillatory structure is observed.<sup>9,10</sup> Thus, the structure in Fig. 1(b) does not truly represent vibrational levels but indicates that the lifetime of the resonance is of the order of the vibrational period of  $N_2$  ( $\sim 10^{-14}$  sec). An estimate of the energy width of the resonance can be obtained by measuring the half width at half maximum on the low-energy side of the first vibrational peak in each excitation function of Fig. 1(b). This measurement yields an approximate energy width (full width at half maximum) of 620 meV which corresponds to a lifetime of  $3 \times 10^{-15}$  sec (i.e.,  $\sim 0.5 \times 10^{-15}$  sec shorter<sup>9</sup> than the  ${}^2\Pi_g$  state of gaseous  $N_2^-$ ).

From the similarity between the gas- and solid-phase resonance parameters, we conclude that, in the film, the combination of Coulomb, exchange, and centrifugal forces which forms a trapping mechanism for the additional electron is only slightly perturbed by the neighboring molecules, whereas the long-range polarization part of the scattering potential is lowered by 0.7 eV by the surrounding media. Since the molecular symmetry is dependent on the short-range portion of the scattering potential, we expect the observed anion to have a symmetry closely related to the gas-phase  ${}^2\Pi_g$  configuration. At monolayer coverages, the estimated width corresponds to the shorter lifetime of  $\sim 5 \times 10^{-16}$  sec. This reduction<sup>11</sup> may result from a severe distortion of the centrifugal barrier and the lowering of the symmetry of the negative ion by the metal surface.

From Fig. 1(b), it can be seen that the positions of the maxima in the oscillatory structure occur at different energies depending on the decay channel. In

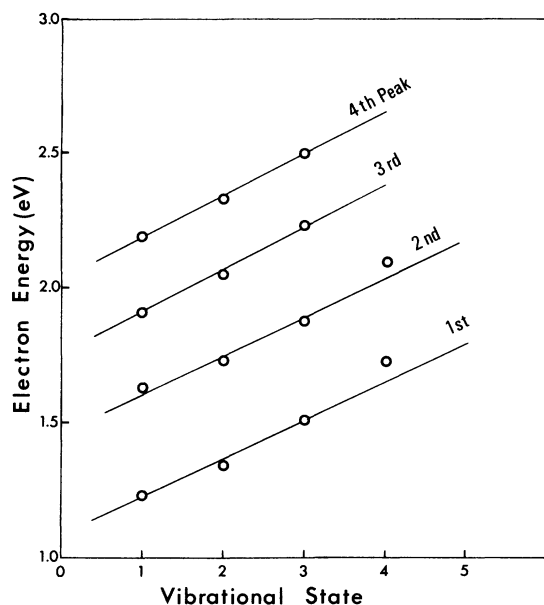


FIG. 2. Energies of 1st, 2nd, 3rd, and 4th peaks in the oscillatory structure of Fig. 1(b) as functions of the quantum number of the final vibrational state. Such an energy dependence of each peak on the decay channel indicates that the lifetime of the  $N_2^-$  state is comparable to the vibrational period.

Fig. 2, the energies of the first four maxima are plotted as functions of the quantum number of each vibrational decay channel. On the basis of a simple long-lifetime model of the formation of the compound state, all the straight lines should be horizontal (i.e., the vibrational peaks of  $N_2^-$  should occur at the

same energy, regardless of the vibrational level of  $N_2$  excited by the *d*-wave resonant electrons). We find here an average increase of 0.16 eV per vibrational state which compares with the gas-phase value of 0.14 eV.<sup>10</sup> This phenomenon, first observed by Schulz,<sup>10</sup> can be explained in terms of the boomerang model formulated by Herzenberg *et al.*<sup>9</sup> The shift is due to the dependence of the lifetime of the anion on its internuclear separation.<sup>4,9</sup> Its observation in the solid definitively characterizes the oscillatory structure in Fig. 1(b) as due to the formation of a quasi-stationary state of  $N_2^-$ , having a lifetime of the order of the vibrational frequency.<sup>9</sup>

In conclusion, the present results establish the existence of a *shape resonance in multilayer  $N_2$  films* whose symmetry is close to the  $^2\Pi_g$  gas-phase counterpart. The *same resonance* has been observed at submonolayer coverages on polycrystalline platinum and silver<sup>2</sup> surfaces. The formation of such transient anion states is expected to play a dominant role in short-range electron scattering from molecules adsorbed or condensed on metal substrates.<sup>12</sup> For  $O_2$  and  $N_2$  deposited on polycrystalline platinum, it has already been shown that these temporary states can enhance the magnitude of vibrational overtones of the fundamental frequency by orders of magnitude.<sup>1,3</sup> The results in  $O_2$  further indicate that electronic excitation cross sections can also be considerably increased by shape resonances.<sup>1</sup>

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