Negative Ion Formation in Adsorbed Molecules: The Role of Surface States

P. J. Rous

Department of Physics, University of Maryland, Baltimore County, Baltimore, Maryland 21228-5398

(Received 27 July 1994; revised manuscript received 10 November 1994)

The formation of negative ions in adsorbed molecules by electron impact is investigated using a layer Korringa-Kohn-Rostoker calculation in which the unoccupied electronic structure of the substrate is fully incorporated. The results reveal a striking enhancement of the cross section for resonance formation caused by the coupling of the molecular resonance to the resonance image states of the substrate. In the case of N_2 physisorbed on Ag(111), this effect greatly increases efficiency of vibrational excitation by electrons that arrive from or detach via the image states of the metal.

PACS numbers: 73.20.Hb

A fundamental aspect of the microscopic description of surface dynamics is the understanding of the formation of transient electronic states of adsorbates and how these excited states couple to inelastic decay channels such as vibrational excitation and dissociative attachment [1,2]. Many electron-induced surface dynamical processes that involve electron attachment to adsorbed molecules are dominated by the formation of molecular negative ions. These processes include photodesorption [3,4], photodissociation [5], molecule-surface scattering [6–8], photon and electron induced oxidation [9], dissociative molecular adsorption [10,11], and dissociative attachment [2,12].

Until recently, all theoretical models of resonance electron scattering by adsorbed molecules have considered only the image interaction between the negative ion and a structureless metallic substrate [13–16]. The interaction between the unoccupied electronic states of the substrate and the molecular resonance has been neglected. This is, in essence, an empty crystal approximation. In this Letter we demonstrate that the substrate electronic structure plays a critical role in determining the cross sections for negative ion formation at surfaces and, consequently, the cross sections for resonant vibrational excitation of adsorbed molecules. In particular, we show that there exist substantial enhancements of the cross section for resonance formation caused by the coupling of the molecular resonance to the (resonance) image states of the substrate.

The results presented in this paper are based upon a recently developed layer Korringa-Kohn-Rostoker (KKR) calculation of resonance formation in adsorbed molecules [17]. The key distinction between this approach and all prior theoretical models of adsorbate resonances is the inclusion of the electronic states of the substrate by a multiple scattering calculation. The method proceeds by computing the energy-resolved scattering matrix, $\tau(E)$, of the surface-molecule system. The resonances of the adsorbed molecule are located by solving the secular equation [18]

$$|1 - SM| = 0, \tag{1}$$

where S and M are the scattering matrices of the surface and molecule, respectively. The root(s) of Eq. (2), which occur at complex energies $E = E_r - i\Gamma/2$, yield the energy E_r and width Γ of the resonance in the adsorbed molecule. The scattering matrix yields the (differential) cross section.

S is evaluated in a mixed plane-wave and angular momentum basis by a layer KKR method [19]. For the surface barrier, we employ the saturated image potential model of Jones, Jennings, and Jepsen [20] fitted by the binding energy of image states [21]. M was determined using a standard scattered-wave $X\alpha$ method [22]. Further details of the computational procedure may be found elsewhere [17,19,23].

We have applied this approach to the calculation of the resonance properties of the $^2\Pi_g$ resonance in N_2 physisorbed on Ag(111). This system was investigated experimentally [24] using high-resolution electron-energy-loss spectroscopy (HREELS). The resonance energy of the adsorbed molecule was found to be $\approx$1.2 compared to 2.3 eV for the free molecule. The resonance lifetime was approximately 40%–80% shorter than that of the free molecule [6]. This system has been the subject of several theoretical studies [15,18,25], all of which employed the empty crystal approximation.

Figure 1 displays the calculated energy and lifetime of the $^2\Pi_g$ resonance in Ag(111)-N_2. For typical physisorption heights, the dominant feature is a reduction of the resonance lifetime and energy in the adsorbed molecule compared to the free molecule. The agreement between the full calculation and empty crystal approximation (Fig. 1) suggests that the dominant effect in determining the resonance lifetime and energy of this low-lying resonance of a *physisorbed* molecule is the screening of the negative ion state by the image potential. When the resonance energy drops below the vacuum level, the resonance survives. When the calculated lifetime and energy are averaged over the variety of sites seen by the physisorbed molecule, we obtain the observed resonance energy and lifetime reduction for adsorption heights of 3–4 Å.

We now consider the cross section for resonance formation in the adsorbed molecule. It is here that the effects of the substrate electronic structure become most apparent. We consider three scattering mechanisms [16]. In

© 1995 The American Physical Society

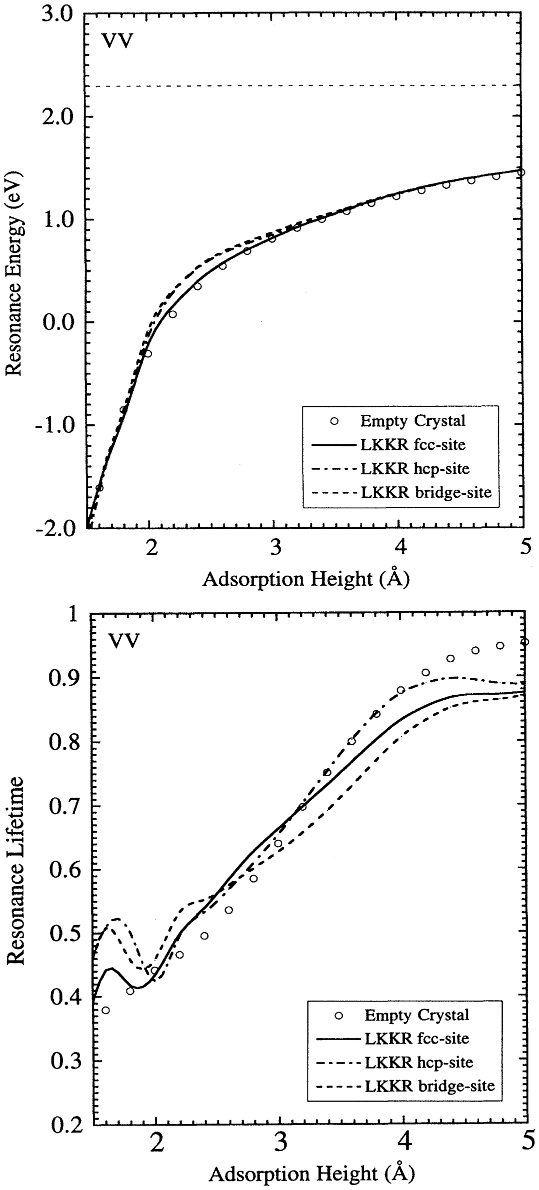

FIG. 1. Calculated energy (a) and lifetime (b) of the $^2\Pi_g$ resonance of N_2 plotted as the function of distance of the molecular center of mass above the first atomic plane of Ag(111). The molecule lies perpendicular to the surface. The lifetime is normalized to the lifetime of the free molecule.

the VV and VM processes the electron is incident upon the surface from the vacuum (V) and is resonantly scattered into the vacuum (VV) or metal (VM). These processes occur in a scattering experiment such as HREELS where the electron arrives from the vacuum with a well-defined energy and angle of incidence. The VM cross section is computed for a fixed angle of incidence (normal to the surface) and is averaged over all detachment angles. In the MM process, electrons are generated in the metal and are resonantly scattered back into the substrate. The MM cross sections are averaged over all angles of incidence and detachment towards or from the metal.

In Fig. 2 we show the calculated MM cross section for resonance scattering by the N_2 molecule adsorbed on Ag(111) via the $^2\Pi_g$ resonance. The total cross sections for elastic scattering, $\nu = 0 \rightarrow 0$ [Fig. 2(a)], and for the excitation of the $\nu = 0 \rightarrow 1$ vibration of molecule [Fig. 2(b)] are shown. The MM cross section is plotted as a function of the resonance energy relative to the vacuum level which decreases as the molecule approaches the surface [see Fig. 1(a)]. We assume that the incident electron energy coincides with the center of the resonance (solid curve).

From Figs. 2(a) and 2(b) we observe a striking feature: When the resonance energy is close to the vacuum level, the cross section exhibits a sequence of sharp peaks where the cross section is enhanced by almost an order of magnitude compared to the free molecule. We find two well-defined peaks at approximately -0.65 and -0.18 eV below the vacuum level, and a small enhancement at approximately -0.1 eV. This sequence of energies is similar to the hydrogenic series, $E_n = -0.85\ \text{eV}/n^2, n = 1, 2, \ldots$, $E_1 = -0.85$ eV, $E_2 = -0.21$ eV, and $E_3 = -0.09$ eV, which suggests that these features are associated with the (resonance) image states of the surface [26,27]. The peaks seen in Fig. 2(a) are close to the binding energies of the image states of the Ag(111) surface: $E_1 = -0.77$ eV (experiment [28]), $E_1 = -0.78$ eV, $E_2 = -0.21$ eV, and $E_3 = -0.09$ eV (theory). To confirm that these features originate from a coupling of the molecular resonance to the image states, the cross section for the excitation of the $\nu = 0 \rightarrow 1$ vibration in the absence of substrate scattering (i.e., for an empty crystal) was computed and is shown in Fig. 2(a). In this case, image states are not supported by the substrate and the oscillatory structure vanishes.

The resonance cross section for excitation of the $\nu = 0 \rightarrow 1$ vibration of molecule is shown in Fig. 2(b). In comparison to the elastic cross section [Fig. 2(a)], two additional peaks appear that are displaced upwards from the image state energies by an amount equal to energy loss suffered by the resonantly scattered electron, $\hbar\omega = 0.28$ eV. Consequently, these additional peaks in the $\nu = 0 \rightarrow 1$ cross section arise from electron *detachment* at an energy that coincides with an image state of the substrate.

According to the phase-shift model [27], an image state is formed by the multiple reflection of an electron between the crystal and the surface barrier. The image states relevant to the results shown in Fig. 3 are associated with the bulk L gap at Ag(111)$\bar{\Gamma}$ that extends below the vacuum level. The localization of an image state just outside the substrate permits the strong coupling to the resonance states of an physisorbed molecule. The oscillatory structure observed in the resonance cross sections is a consequence of the rapid modulation of the substrate local density of states (and therefore the

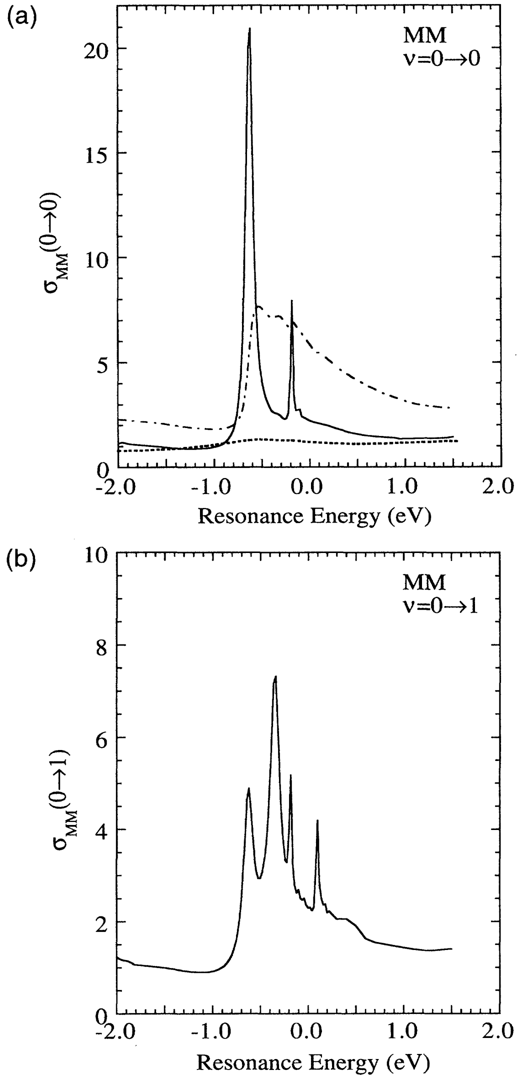

FIG. 2. The calculated MM cross section of the ${}^2\Pi_g$ resonance of N_2 adsorbed above the fcc-hollow site of Ag(111) (a) for elastic scattering, $\nu = 0 \rightarrow 0$. (b) For the excitation of the $\nu = 0 \rightarrow 1$ vibration $\Delta E = \hbar\omega = -0.28$ eV. Solid line: full; layer KKR calculation. Dashed line: empty crystal. Dot-dashed line: MM cross section that would be observed in a hot electron experiment. The cross sections are normalized to those of the free molecule.

tunneling rate) as the electron energy tranverses the Rydberg series.

In a hot electron experiment, the electrons are emitted from the substrate with a distribution of kinetic energies: $E \leq E_{\max} = E_F + h\nu$. In order to simulate such an experiment, the MM cross section shown in Fig. 2(a) (solid curve) was averaged over the resonance profile for $E \leq E_F$ and plotted in Fig. 2(a) (dot-dashed curve). The effect of averaging is to broaden the features observed for a monochromatic electron source so that the enhancements due to the individual image states cannot be resolved. However, the influence of coupling to image states remains by enhancing the MM cross section (×3) close to the vacuum level.

Although the image states exist only below the vacuum level, they can influence the cross sections for vibrational excitation stimulated by electrons incident from the vacuum where the electron has a well-defined energy and angle of incidence. Figure 3 shows the calculated total VM cross section for excitation of the $\nu = 0 \rightarrow 0\text{–}6$ vibrations by electrons incident normal to the surface. Significant enhancements in the cross sections appear above the vacuum level when higher order vibrations are excited. For example, the $\nu = 0 \rightarrow 5$ excitation is enhanced at three energies which correspond to detachment of the electron into the image states below the vacuum level; the peak at approximately +1.2 eV is created by detachment into the $n = 2$ image state at $E_2 \approx (1.2 - 5)\hbar\omega \approx -0.2$ eV.

The modulation of the resonance cross sections caused by coupling to the image states has profound implications for the resonant vibrational excitation of adsorbed molecules. Figure 4 shows the cross section for vibrational excitation of physisorbed N_2 on Ag(111) via the VV, VM, and MM processes. While the VV cross section decreases monotonically with ν [6], both the VM and MM cross sections show significant enhancements of the higher order ($\nu = 5, 6, 7$) overtones. For the VM and MM processes, the calculated $\nu = 0 \rightarrow 5$ cross section is almost 2 orders of magnitude larger than for the VV process and is similar in magnitude to the excitation cross section of the free molecule. This enhancement occurs because the electron that detaches from the molecule having excited a $\nu = 0 \rightarrow 5$ vibration is captured by the $n = 2$ image state of the Ag(111) substrate.

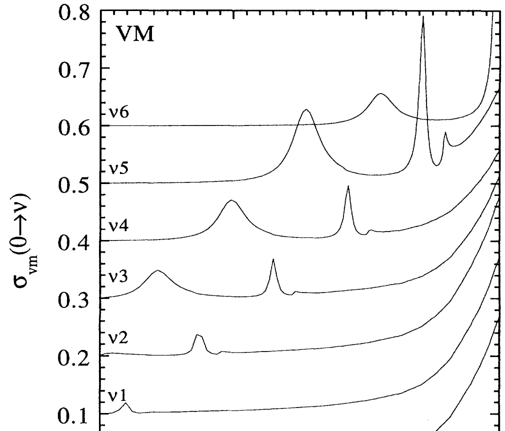

FIG. 3. As Fig. 2, but for the calculated VM cross sections of elastic scattering, $\nu = 0 \rightarrow 0$, and for the excitation of the $\nu = 0 \rightarrow 1$ to $\nu = 0 \rightarrow 6$ vibrations. Each curve is shifted vertically by 0.1; when the resonance energy is zero, the VM cross sections for all decay channels are zero.

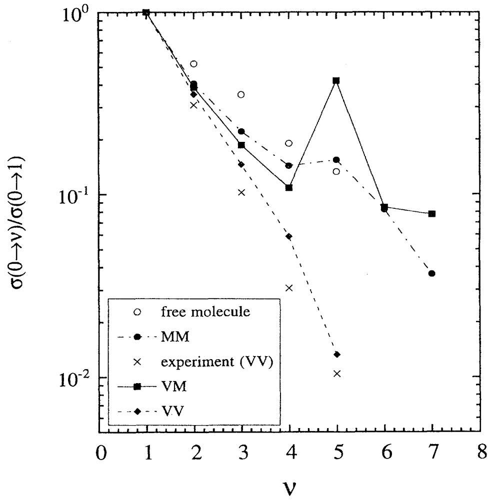

FIG. 4. Calculated cross sections for vibrational excitation of overtones of physisorbed N_2 on Ag(111) via the VV, VM, and MM processes, normalized to the cross section of the $\nu = 0 \rightarrow 1$ excitation. The overtone spectrum for the free molecule and adsorbed molecule is also displayed [24].

The behavior we have observed will not be confined to the N_2-Ag(111) system considered here. Image states are a common feature of many metallic surfaces [21,27], and coupling to both atomic and molecular resonances is possible. In order for cross-section enhancements via direct population of image states to be important, the resonance energy of the adsorbed molecule must be equal to the sum of a few vibrational quanta. Nevertheless, it may be possible to observe enhanced resonance formation for higher-energy resonances if the image states can be coupled to the resonance by diffraction [29]. The MM processes we have described can be stimulated by hot electrons generated, for example, by substrate photoexcitation. Since photoexcitation generates electrons with a distribution of kinetic energies, sharp enhancements of the MM cross sections may not be resolved directly in a hot electron experiment unless the resonance width is smaller than a few tenths of an eV. These enhancements of resonance formation by substrate scattering alter not only the probability of vibrational excitation but may also influence other resonance-enhanced dynamical processes such as electronic excitation, desorption, and dissociation.

This research was supported by the National Science Foundation Division of Materials Research, DMR-9319436, and the Donors of The Petroleum Research Fund, administered by the American Chemical Society.

[1] R.E. Palmer, Prog. Surf. Sci. **41**, 51 (1992).
[2] L. Sanche Comments At. Mol. Phys. **26**, 321 (1991); J. Phys. B **23**, 1597 (1990).
[3] J.W. Gadzuk, L.J. Richter, S.A. Buntin, R.R. Cavanagh, and D.S. King, Surf. Sci. **235**, 317 (1990).
[4] X.-L. Zhou, X.-Y. Zhu, and J.M. White, Surf. Sci. Rep. **13**, 73 (1991).
[5] J. St. Dixon-Warren, E.T. Jensen, and J.C. Polanyi, J. Chem. Phys. **98**, 5938 (1993).
[6] J.W. Gadzuk, Annu. Rev. Phys. Chem. **39**, 395 (1988).
[7] P. Haochang, T.C.M. Horn, and A.W. Kleyn, Phys. Rev. Lett. **57**, 3035 (1986).
[8] A.W. Kleyn,Vacuum **41**, 248, (1990).
[9] Y. Chen, Y-S. Luo, J.M. Suo, and J.H. Weaver, Phys. Rev. B **43**, 4527 (1991).
[10] S. Holloway and J.W. Gadzuk, J. Chem. Phys. **82**, 5203 (1985).
[11] P.J. van der Hoek and E.J. Baerands, Surf. Sci. Lett. **221**, L791 (1989).
[12] L.A. Silva and R.E. Palmer, Surf. Sci. **272**, 313 (1992).
[13] R.E. Palmer and P.J. Rous, Rev. Mod. Phys. **64**, (1992).
[14] D. Teillet-Billy and J.P. Gauyacq, Nucl. Instrum. Methods **58**, 393 (1991).
[15] D. Teillet-Billy, V. Djamo, and J.P. Gauyacq, Surf. Sci. **269/270**, 425 (1992).
[16] V. Djamo, D. Teillet-Billy, and J.P. Gauyacq, Phys. Rev. Lett. **71**, 3267 (1993).
[17] P.J. Rous, Surf. Sci. Lett. **279**, L191 (1992).
[18] A. Gerber and A. Herzenberg, Phys. Rev. B **31**, 6219 (1985).
[19] J.M. Maclaren, S. Crampin, and D.D. Vvedensky, Phys. Rev. B **40**, 12 164 (1989).
[20] R.O. Jones, P.J. Jennings, and O. Jepsen, Phys. Rev. B **29**, 6472 (1984).
[21] N.V. Smith, C.T. Chen, and M. Weinert, Phys. Rev. B **40**, 7565 (1989).
[22] D. Dill and J.L. Dehmer, J. Chem. Phys. **61**, 692 (1974).
[23] P.J. Rous (to be published).
[24] J.E. Demuth, D. Schmeisser, and Ph. Avouris, Phys. Rev. Lett. **47**, 1166 (1981).
[25] P.J. Rous, Surf. Sci. **260**, 361 (1992).
[26] S.D. Davison and M. Steslicka, *Basic Theory of Surface States* (Oxford, New York, 1992).
[27] P.M. Echenique and J.B. Pendry, Prog. Surf. Sci. **32**, 111 (1990).
[28] K. Giesen, F. Hage, F.J. Himpsel, H.J. Reiss, and W. Steinmann, Phys. Rev. B **35**, 971 (1987).
[29] R.O. Jones and P.J. Jennings, Surf. Sci. Rep. **9**, 165 (1988).