Resonant Vibrational Excitation of Adsorbed Molecules by Electron Impact

V. Djamo,* D. Teillet-Billy, and J. P. Gauyacq
Laboratoire des Collisions Atomiques et Moléculaires, Université de Paris-Sud, Bâtiment 351, 91405 Orsay Cedex, France
(Received 2 April 1993)

The vibrational excitation of N_2 molecules adsorbed on a silver surface by low energy electron impact is studied within the newly developed coupled angular mode method. The process involves the formation of a transient negative molecular ion. The results account well for the observations of Demuth and co-workers. They also reveal that most of the vibrational excitation corresponds to electrons scattered into the metal and thus unobservable in a scattering experiment.

PACS numbers: 34.80.Gs, 79.20.−m

The energy transfer between the electronic and nuclear motions in the course of an electron molecule is rather difficult due to the large mass ratio between electrons and nuclei. The situation is completely different if the incident electron can be captured by the target molecule to form a transient negative molecular ion. In gas-phase collisions, vibrational excitation at low energy is very often dominated by resonant processes [1]:

$$e^- + AB \rightarrow AB^{-*} \rightarrow e^- + AB^*(v) .$$

The same kind of arguments hold for molecules adsorbed on a metal surface and indeed, resonant scattering is an important source of vibrational excitation. It was first observed in 1981 by Demuth and co-workers [2] and Sanche and Michaud [3]. In fact, the formation of transient negative ions enables an efficient energy transfer between electrons and nuclei and it has been invoked as an intermediate step in a variety of processes involving metal surfaces and molecules: desorption by electron impact [4], photodesorption [5], reactivity [6], and electronic deexcitation [7,8]. Studies of resonant scattering have also revealed that transient negative ions could be used as a probe of the molecule environment [9]. The possibility for a quantitative discussion of all the above processes depends on the availability of an accurate treatment of the resonant energy transfer. In the present paper, we report on the first study of the dynamics of vibrational excitation in electron collisions with adsorbed molecules that quantitatively takes into account the presence of the metal surface. It is applied to N_2 molecules physisorbed on silver and it reveals some unexpected features on the importance of the vibrational excitation process. The N_2 molecule and its $N_2^-(^2\Pi_g)$ resonance have been studied extensively in the gas phase: The resonance is located around 2.3 eV and is associated with an $l=2$ wave. For adsorbed molecules, Demuth and co-workers [2] observed the same resonance, however, modified by the metal environment: The resonance energy is lowered, the oscillating structure of the cross section as a function of the energy has disappeared, and the overtone excitation is decreased. Similar results were observed for thick layers of N_2 molecules condensed on other metals [10,11]. Since these pioneering works, resonant vibrational excitation has been observed in quite a few systems; they have been recently reviewed in [11,12]. Theoretical studies on this problem are more scarce. The first ones [13,14] studied vibrational excitation using simplified models with adjusted parameters: constant adjusted resonance lifetime with an unperturbed resonance energy in [13], and gas-phase-like calculation with unperturbed energy in [14]. They do not report on vibrational excitation cross sections but rather concentrate on the overtone excitation ratios. As the main result, they stress the shortening of the resonance lifetime and the lowering of the resonance energy upon adsorption. More recently studies [15,16] of the static molecule-surface systems were performed with the coupled angular mode (CAM) methods [17]: They computed the width and position of the molecular resonances as a function of the molecule-surface distance. Such a static calculation, i.e., with a fixed internuclear distance, is limited to qualitative discussions of the problem. In the present work, we report on a dynamical calculation of the vibrational excitation process, fully taking into account the vibrational motion of the molecule.

The calculation is performed within the CAM formalism [17], properly generalized to handle the molecular vibrational motion. The CAM method was developed to study atomic and molecular levels in front of metal surfaces. It was applied to various problems: negative ion formation in atom-surface scattering [18], quenching of excited states [8], static calculation of negative molecular ion levels [15,16], and the study of neutral systems [19]. The CAM method considers the scattering of the collisional electron by the compound system consisting of the neutral target molecule and the metal surface. Such a method applies to physisorption situations where one can assume that the target molecule is not much perturbed by the presence of the metal. The electron-metal surface interaction is represented by a local potential [20], the only function of z the electron-surface distance. The electron-molecule interaction is modeled by the effective range approximation (ERT; see, e.g., in Ref. [21]), which was developed to study inelastic processes (vibrational and electronic excitation) in low energy electron-molecule collisions. The ERT description of the N_2^- resonance was extracted from the ionic potential energy curves of Dubé and Herzenberg [22]. In the CAM method, the electron scattering wave function is described by a close coupling expansion over spherical harmonics Y_{lm} centered around the molecule:

$$\Psi=\sum_v\sum_l\frac{1}{r}F_{lv}(r)Y_{lm}(\theta,\varphi)\chi_v(R)\,,$$

where $\chi_v(R)$ is the target molecule vibrational wave function (v level), r,θ,φ are the electron spherical coordinates, and $F_{lv}(r)$ is the electron radial wave function.

The molecular axis is supposed to be fixed in space (perpendicular to the surface in the present study). The above expansion is well suited to treat the electron-molecule interaction and not the electron-surface interaction. The latter introduces coupling terms between the various angular modes. When brought into the Schrödinger equation, this expansion leads to the set of the CAM coupled equations for the $F_{lv}(r)$, which have to be solved together with the ERT boundary condition. This treatment can be seen as an extension to an anisotropic environment of the ERT treatment developed for gas-phase collisions. The approximation lies in the representation of the e^--fixed R molecule interaction, and after that, it exactly treats the dynamics of the vibrational excitation with all its dynamical and nonlocal effects [21]. Details about the calculations will be published elsewhere [23]. The calculation of differential cross sections as functions of the incident and exit angles would require a very large number of angular momenta in the above expansion. In the present work, we rather computed four different "summed" cross sections labeled VV, VM, MV, and MM (V stands for vacuum and M for metal); they are defined as the integrals of the differential cross section over the incident *and* final angles, restricted to a given region of space: metal or vacuum. The first letter refers to the integration domain for the incident angle and the second one for the exit angle. In gas-phase collisions, for freely rotating molecules, each of these four summed cross sections is equal to one-fourth of the total cross section. These summed cross sections correspond to an average over the angle; they measure the importance of the vibrational excitation, as well as the relative weight of the vacuum and metal sides in the process. Indeed, the VV process corresponds to a scattering experiment like that of Demuth and co-workers, who measured the scattered intensity at a fixed scattering angle. In the following, the VV results will be compared to the results of Demuth and co-workers; indeed, the angular distribution of scattered electrons that is characteristic of the resonant process should not vary much with the collision energy. The VM process is present in the same experimental situation but is unobservable in a scattering experiment. The MV and MM processes are related to hot electrons incident from the metal side and could then be related to experiments with photoexcited electrons. Two different methods were used to compute the summed cross sections from the solution of the coupled equations. In the first one, we first calculate the total inelasticity, i.e., the sum of all the squared modulus of the inelastic S matrix elements; for each $0\rightarrow v$ transition (sum of VV, VM, MV, and MM processes) it very quickly converges with the number of angular waves (typically nine). The separation of the V and M contributions is made via a classical mechanics calculation: Since the $^2\Pi_g N_2^-$ resonance is an $l=2$ resonance, we compute by classical mechanics the fractions of the electrons emitted from the molecule according to a $d\pi$ wave that are deflected by the e^--surface interaction potential and end up in the vacuum or metal sides. These fractions are used to share the total inelasticity among σ_{VV}, σ_{VM}, σ_{MV}, and σ_{MM}. In a second calculation, the V-M separation was made in the scattering calculation: The S matrix is computed in an adiabatic angular basis obtained by diagonalizing the e^--surface potential in the Y_{lm} basis [15]. Certain vectors correspond to the vacuum and others to the metal side; however, at finite distances, other vectors are localized close to the surface. Because of the image forces and the low energy of the electron, an electron close to the surface at finite distance will end up in the metal at infinity. Computation of the summed cross section with a separation (metal + surface and vacuum) of the adiabatic basis leads to results close to the classical separation [23]. The latter are presented below.

Figure 1 presents results for the $v=0\rightarrow v=1$ resonant vibrational excitation of N_2 as a function of the collision energy. The gas-phase total cross section is presented in Fig. 1(a); it is very close to the theoretical and experimental results [22]. It displays the well known "boomerang oscillations," due to the nuclear motion in the N_2^- collision intermediate. Figure 1(b) shows the summed cross section σ_{VV} (for a molecule-surface distance of $5a_0$) compared with the normalized experimental results of Demuth and co-workers [2]. A good overall agreement is obtained. A few features are apparent: First, the resonance is shifted to lower energies compared to its gas-phase position. Second, the boomerang oscillations have almost disappeared; this is a consequence of the shortening of the resonance lifetime. These changes in the resonant position and lifetimes were apparent in the qualitative discussions drawn from the static calculations [15]. They were mainly attributed to the interaction of the collisional electron with its electrical image which lowers the energy and attracts the electron towards the metal. The changes in the cross section [Fig. 1(b) compared to Fig. 1(a)] are indeed dependent on Z the molecule-surface distance. This evolution will be presented elsewhere [23]. In the present work, we chose a molecule-surface distance of $5a_0$ (measured from the image reference plane) as representative of the range where the theoretical results most resemble the experimental results. It is a quite reasonable value for a physisorption distance. The absolute value of the $v=0\rightarrow v=1$ excitation cross section is also significantly decreased compared to its value for a free molecule: The maximum cross section is decreased by a factor 10, although the incident energy is decreased by a factor 2. It is noticeable that a rather substantial change of the shape of the cross section [Figs. 1(a) and 1(b)] corresponds to a rather moderate apparent increase

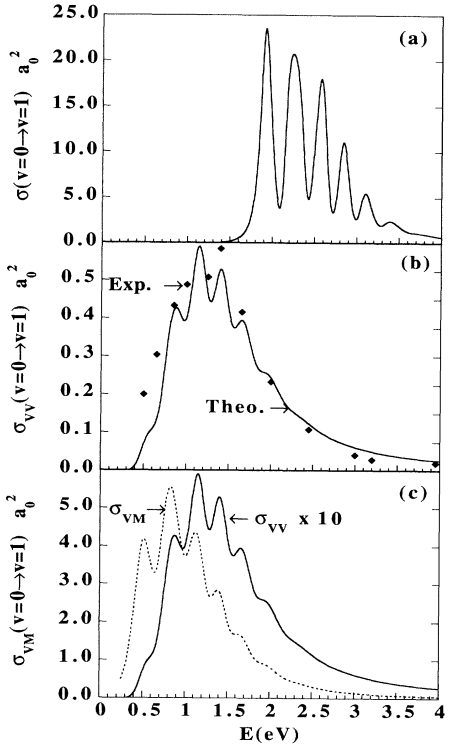

FIG. 1. Cross sections for the vibrational excitation ($v=0 \rightarrow v=1$) of the N_2 molecule as a function of collision energy. (a) For an isolated molecule. (b) Vacuum-vacuum cross section for a molecule adsorbed on a silver surface, (◆) experimental results [2]. (c) Vacuum-metal and vacuum-vacuum cross sections.

of the resonance width (40% at R_e, the equilibrium position of N_2 [15]). In fact, the target molecule vibrates during the excitation process and then it samples a range of internuclear distances R. In the gas phase, for R increasing from R_e, the width decreases and even vanishes. For adsorbed molecules, the static calculations [15] have shown that the width does not vanish anymore, even when the resonance is below the vacuum level: The electron can always escape toward the metal. As a consequence, the relative increase of the resonance width upon adsorption is much more important at large R and accounts for the observed variation of shape of the excitation cross section. Figure 1(c) reveals a new feature: The comparison between σ_{VV} and σ_{VM} shows that vibrational excitation predominantly corresponds to electrons leaving the molecule on the metal side. So, for the experimental situation of a scattering experiment, most of the vibrational excitation process cannot be observed. This is mostly an energy effect. Indeed, when the outgoing electron leaves the molecule, it feels the e^--surface interaction which attracts it toward the metal. Depending on its ejection energy and angle, the electron will or will not have enough energy to overcome the surface barrier. The angular criterion is linked with the present description using a surface potential; a more sophisticated treatment including

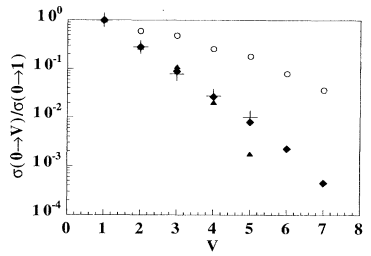

FIG. 2. Overtone excitation: (+) experimental results [2] and (○) theoretical results for an isolated molecule; theoretical results for an adsorbed molecule from VV cross sections (▲) at fixed incident energy (1.5 eV) and (◆) at the cross section maximum.

the crystallographic structure [24] could lead to a surface reflectivity different from the present one and this will influence the angular criterion. Indeed, the energy criterion, which is very important for the overtone excitation, is not influenced by the surface description. The ratio between the VV and VM processes depends on the collision energy: The smaller the incident energy, the larger the ratio between σ_{VM} and σ_{VV}. This ratio even becomes infinite below the threshold for the VV process; indeed, the VM process does not have an energy threshold in this range since an electron escaping into the metal will gain an energy equal to the potential inside the metal that is much larger than the excitation energies considered here.

Resonant vibrational excitation is very efficient in exciting a few quanta of vibration in a unique collision. Figure 2 presents the relative values of σ_{VV} for the different vibrational channels. The σ_{VV} are taken either at a fixed incident energy (1.5 eV to compare with Demuth and co-workers' results) or at the cross section maximum which is a better estimate of the importance of the process. These two definitions of the overtone excitation are very close to each other except for $v=5$, which is very close to its threshold at 1.5 eV. Here again, the present results agree with the experimental data [2]. It is noteworthy that although still important, the overtone excitation is significantly smaller for adsorbed molecules than for free molecules. This feature was attributed to

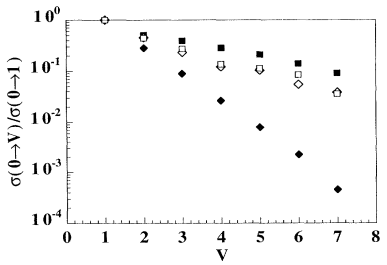

FIG. 3. Overtone excitation (theoretical): ◆ from VV cross sections; ■ from VM cross sections; and ◇, □ with degenerate levels.

the shortening of the resonance lifetime due to the interaction with the surface [13,14]. The interpretation is a little more intricate. Indeed, Fig. 3 presents the comparison between the overtone excitation in the VV and VM processes. The overtone excitation appears to be extremely efficient in the VM case; it is comparable to that of the free molecule case, although the resonance lifetime has significantly shortened. The resonance lifetime is not the only factor acting on the overtone excitation and in the present case a strong energy effect is also present. Indeed, for the VV or for the gas-phase problem, the excitation of high lying v levels has a rather high energy threshold (e.g., 1.68 eV for $v=6$). This threshold does not exist for the VM process. For $Z=5a_0$, the resonance position is around 1 eV as well as the maximum of σ_{VM} ($v=0\rightarrow v=6$). However, for σ_{VV} ($v=0\rightarrow v=6$), the resonance being around 1 eV and the threshold around 1.68 eV, the cross section is very small close to threshold and its maximizes around 2.2 eV, i.e., in a region which is rather far away in the wings of the resonance. The same effect is already visible in $v=0\rightarrow v=1$ excitation [Fig. 1(c)], where the two summed cross sections appear shifted. The drop of the overtone excitation in the VV process thus appears to be due to a resonance position shifted below the energy threshold of the high overtones; the VM process does not have this restriction and the overtone excitation is strong. This interpretation has been checked by making a test calculation in which all the various v levels are supposed to have the same energy, in order to remove all these energy effects. The corresponding results are shown in Fig. 3; the overtone excitation is now strong in both σ_{VM} and σ_{VV}. The roughly constant overtone excitation when going from the free molecule to the VM case thus comes from the approximate cancellation of two opposite effects: the increase of the resonance width and the removal of thresholds. This new result on the overtone excitation has two interesting aspects which should be stressed. First, molecules adsorbed on a metal can be excited very efficiently by electrons with an *incident energy below the energy threshold*; the missing energy comes from the fact that the collisional electron ends up in a negative energy state, i.e., is trapped in the metal. Second, the vibrational excitation, when observed in a scattering experiment, is largely underestimated; if one refers to the maximum of the cross sections in the present N_2/Ag case, the hidden cross section (σ_{VM}) is 10 times larger than the visible one (σ_{VV}) for the $v=0\rightarrow 1$ excitation and 2×10^3 times larger for the $v=0\rightarrow 7$ excitation.

In conclusion, the resonant vibrational excitation of N_2 molecules adsorbed on Ag by electron impact was studied within the CAM formalism. The results stress two important features of the modification of the N_2^- resonant state upon adsorption: Its energy is lowered and its lifetime is decreased. These features account well for the experimental observations of Demuth and co-workers [2]. A new feature is revealed by the present calculation: For electrons incident from the vacuum, most of the vibrational excitation process corresponds to electrons scattered into the metal and thus unobservable in scattering experiment. This tendency is particularly important for the overtone excitation. The energy transfer between the incident electron and the vibrational motion of the target is much more important than thought before. This large energy transfer could show up either in experiments involving hot electrons (for example, created by photon absorption) or indirectly via the effect of the vibrational excitation on other processes: reactivity, desorption, etc.

Laboratoire des Collisions Atomiques et Moléculaires, Université de Paris-Sud is URA associée au CNRS No. 281.

*Also at Institute of Atomic Physics, Bucarest, Romania.

[1] G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).
[2] J. E. Demuth, D. Schmeisser, and Ph. Avouris, Phys. Rev. Lett. **47**, 1166 (1981); D. Schmeisser, J. E. Demuth, and Ph. Avouris, Phys. Rev. B **26**, 4857 (1982).
[3] L. Sanche and M. Michaud, Phys. Rev. Lett. **47**, 1008 (1981).
[4] R. Azria, L. Parenteau, and L. Sanche, Phys. Rev. Lett. **59**, 638 (1987).
[5] J. W. Gadzuk, L. J. Richter, S. A. Buntin, D. S. King, and R. R. Cavanagh, Surf. Sci. **235**, 317 (1990).
[6] J. W. Gadzuk, Comments At. Mol. Phys. **16**, 219 (1985).
[7] R. Hemmen and H. Conrad, Phys. Rev. Lett. **67**, 1314 (1991).
[8] A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, Surf. Sci. **284**, 337 (1993).
[9] R. E. Palmer, R. J. Rous, J. K. Wilkes, and R. F. Willis, Phys. Rev. Lett. **60**, 329 (1988).
[10] M. Bertolo and K. Jacobi, Surf. Sci. **265**, 12 (1992).
[11] L. Sanche, J. Phys. B **23**, 1597 (1990).
[12] R. E. Palmer and P. J. Rous, Rev. Mod. Phys. **64**, 383 (1992).
[13] J. W. Gadzuk, J. Chem. Phys. **79**, 3982 (1983).
[14] A. Gerber and A. Herzenberg, Phys. Rev. B **31**, 6219 (1985).
[15] D. Teillet-Billy and J. P. Gauyacq, Nucl. Instrum. Methods Phys. Res., Sect. B **58**, 393 (1991); D. Teillet-Billy, V. Djamo, and J. P. Gauyacq, Surf. Sci. **269/70**, 425 (1992).
[16] P. J. Rous, Surf. Sci. **260**, 361 (1992).
[17] D. Teillet-Billy and J. P. Gauyacq, Surf. Sci. **239**, 343 (1990).
[18] A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, Phys. Rev. Lett. **68**, 2842 (1992); Surf. Sci. **278**, 99 (1992).
[19] A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, Nucl. Instrum. Methods Phys. Res., Sect. B (to be published).
[20] P. J. Jennings, R. O. Jones, and M. Weinert, Phys. Rev. B **37**, 6113 (1988).
[21] J. P. Gauyacq, *Dynamics of Negative Ions* (World Scientific, Singapore, 1987); D. Teillet-Billy and J. P. Gauyacq, J. Phys. B **17**, 4041 (1984); D. Teillet-Billy, L. Malegat, and J. P. Gauyacq, J. Phys. B **20**, 3201 (1987).
[22] L. Dubé and A. Herzenberg, Phys. Rev. A **20**, 194 (1979).
[23] V. Djamo, D. Teillet-Billy, and J. P. Gauyacq (to be published).
[24] P. J. Rous, Surf. Sci. **279**, L191 (1992).