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# Low-energy electron scattering by $N_2$ molecules physisorbed on Ag: Study of the resonant vibrational excitation process

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Molecules adsorbed on a metal surface can be excited by low-energy electron impact. Resonant processes in which an intermediate negative ion is formed during the collision are very efficient. The resonant vibrational excitation of $N_2$ molecules physisorbed on Ag by low-energy electrons is studied theoretically with the coupled-angular-mode method. The influence of the neighboring surface on the excitation process (including the excitation of overtones) is analyzed. The results are compared with the experimental results of Demuth, Schmeisser, and Avouris. It is found that in a scattering experiment, most of the vibrational excitation concerns electrons that are inelastically scattered into the metal and are thus not observed experimentally.

## I. INTRODUCTION

In the course of an electron-molecule collision, the large mass ratio between the electron and the nuclei makes an energy transfer between the electronic and nuclear motion and hence the vibrational excitation very unlikely. However, if there exists a trapping phenomenon for the incident electron, i.e., if it can be captured by the target molecule to form a temporary negative molecular ion, then the increase of the collision time strongly facilitates the energy transfer between the electron and the nuclei. This process, known as resonant scattering, was recognized in the 1970s as being very important for vibrational excitation in low-energy electron-molecule collisions:[1]

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

This process is usually characterized by rather large excitation cross sections in a well-defined incident electron energy range, by a large efficiency for exciting high-lying vibrational levels and by angular distributions of the scattered electrons that are characteristic of the symmetry of the involved intermediate ion. Resonant vibrational excitation is well documented for free molecules. It has also been observed for molecules adsorbed on surfaces. Following the pioneering works of Sanche and Michaud[2] and Demuth, Schmeisser, and Avouris,[3] numerous studies of this process for various molecules have been reported; they have been reviewed by Sanche[4] and by Palmer and Rous.[5] The resonances were found to dominate vibrational excitation in low-energy collisions. They were also seen to lead to electronic excitation[6] similarly to the case of free molecules;[7] they also lead to a process specific to adsorbed molecules: the excitation of the relative molecule-surface movement.[8]

Most interpretations for resonant scattering by adsorbed molecules were done by comparison with a similar process for free molecules. Indeed, for physisorbed molecules, the distortions introduced by the surface are weak, and one can expect that the same resonances will show up in free and adsorbed molecules. For chemisorbed molecules, the situation is more complex: the changes of the electronic structure of the molecules introduced by the adsorption are more important, in particular a charge transfer between the surface and the molecule is possible, and all this can modify the scattering properties. Nevertheless, discussions of the evolution of resonant scattering under adsorption could be presented.[9] For molecules physisorbed on metals, which is the case for the present study, the metal surface environment modifies the resonance characteristics. Qualitatively, the electron-surface interaction, which reduces to the image charge interaction at large electron-surface distances, attracts the extra electron of a molecular negative ion. As recognized in experimental[2,3] and model studies[10,11] of this problem, this leads to a lowering of the resonance positions and to a decrease of their lifetime. The same interaction also modifies the angular distributions for resonant scattering[12] together with multiple-scattering effects.[13] Only a few theoretical studies of the resonant scattering problem for adsorbed molecules have been reported, most of them on the $N_2$ molecule. That by Gadzuk[10] made use of a simplified model of vibrational excitation with adjustable parameters; it discussed the various aspects of the process, and stressed the importance of the decrease of the resonance width in the interpretation of the experimental results of Demuth, Schmeisser, and Avouris[3] ($N_2$ physisorbed on Ag). Gerber and Herzenberg[11] performed two models studies: one on the static problem (molecule with fixed nuclei), which showed that due to the coupling with the surface the resonance width increases, and that due to the image charge interaction the resonance energy is lowered. In a second study, starting from a modeling of the electron-free $N_2$ system, they simply changed the resonance lifetime by an adjusted constant and showed that a decrease of the resonance lifetime could reproduce the experimental results of Demuth, Schmeisser, and Avouris[3] and Schmeisser, Demuth, and Avouris[14] on the overtone excitation. More recently, two similar studies

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of the static $N_2$/Ag problem[15,16] were performed using the coupled-angular-mode (CAM) method.[17] In a unique nonperturbative calculation they confirmed the evolution of the resonance characteristics when a $N_2$ molecule approaches a metal surface: decrease of the resonance energy and increase of its width. Rous[18] also performed a study of the effect of the surface cristallographic structure on the resonant scattering, and concluded the absence of a sizable effect for the $N_2$/Ag system. These studies confirmed the previous model studies; however, they were only static studies, since they treat electron scattering by a $N_2$ molecule at a *fixed* internuclear distance. Such studies can only yield static resonance characteristics and cannot make quantitative predictions for the vibrational excitation problem.

Recently,[19] we extended the CAM method to treat the dynamical problem, i.e., the resonant electron scattering by a vibrating molecule physisorbed on a metal surface. This yielded quantitative predictions for the vibrational excitation process. The present work is devoted to the case of $N_2$ molecules adsorbed on Ag, studied experimentally by Demuth, Schmeisser, and Avouris.[3] We study the low-energy range (0 to a few eV), where the $^2\Pi_g$ resonance[20] is located. This resonance, located around 2.3 eV for the free molecule, has been studied extensively by gas-phase experiments and theoretical approaches.[21–25] It corresponds to the case of an intermediate width, its lifetime being of the same order of magnitude as the $N_2$ vibrational period; this situation leads to the well-known boomerang situation,[24] and can thus be expected to be very sensitive to the environment.

## II. METHOD

### A. Coupled-angular-mode (CAM) method

In the present work, we use an extension of the CAM method that can handle the vibrational motion of the target molecule. The basic idea of the CAM method[17] is to study electron scattering by a compound interaction formed by the superposition of the electron-molecule and electron-surface interactions. They are supposed not to be perturbed one by the other, and this limits the applicability of the method to large distances, i.e., to the physisorption case. The CAM method has been applied to various problems: determination of atomic level characteristics for studies of the charge-transfer process in atom-surface interaction,[17] study of the dynamical charge-transfer problem,[26] studies of positions and widths of molecular ion resonances,[15] and studies of reactions induced by a charge transfer.[27]

The electron-surface interaction is described by a local potential only function of $z$, the electron-surface potential. For the Ag surface, we used the potential given by Jennings, Jones, *et al.* and Weinert:[28]

$$\begin{aligned} V_S &= -\frac{1}{4z}(1-e^{-\lambda z}), \quad z>0 , \\ V_S &= -U_0/(1+Ae^{Bz}), \quad z<0 , \end{aligned} \tag{1}$$

with $\lambda=0.97a_0^{-1}$ and $U_0=13.74$ eV ($A$ and $B$ are such that $V$ and $dV/dz$ are continuous in $z=0$).

The electron-molecule interaction is described in the effective range approximation (ERT).[29] It assumes that the scattering can be described by uncoupled angular modes (spherical harmonics in the present case). The long-range electron-molecule interaction is described by a local potential $V_{lm}^{\text{ext}}(r)$, a function of the electron-molecule distance $r$. This potential depends on the angular mode considered $(l,m)$, and it incorporates the centrifugal term. The short-range interactions are represented by a boundary condition at $r=r_c$ on the electron radial wave function $\psi_{lm}$ for each angular mode $(l,m)$:

$$\left.\frac{1}{\psi_{lm}}\frac{\partial\psi_{lm}}{\partial r}\right|_{r=r_c} = f_{lm} . \tag{2}$$

This boundary condition which depends on the target molecule internuclear distance $R$ is assumed to be energy independent in the limit of low-energy scattering; this is justified by the fact that the electron experiences very large potentials in the inner region $(r<r_c)$, much larger than its asymptotic energy. This boundary condition can either be extracted from *ab initio* calculations or be adjusted to reproduce some known quantities.

In the present study, the $N_2^-(^2\Pi_g)$ resonance is associated with an $l=2$, $m=1$ ($d\pi$) wave. The ERT boundary condition (2) for the resonant $d\pi$ wave, which depends on the target molecule internuclear distance, was chosen to reproduce the theoretical results of Dubé and Herzenberg on $e^-$-free $N_2$ collisions:[25] at each internuclear distance $R$, the boundary condition $f_{21}$ was adjusted so that the position of the $N_2^-$ $(^2\Pi_g)$ resonance, coming out of the ERT approach, reproduces that of the work of Dubé and Herzenberg.[25] For $r_c=1.4$ a.u., the boundary condition is given by

$$f_{21} = -0.117-0.474(R-R_e)+0.314(R-R_e)^2 ,$$

where $R_e$ is the $N_2$ internuclear equilibrium distance.

The boundary condition for the nonresonant waves was adjusted to phase shifts taken from Refs. 30 and 31 and assumed to correspond to free waves for the higher angular momenta. These other waves do not correspond to a resonant mode, and the boundary condition is taken to be independent of $R$. This approximation neglects the nonresonant part of the vibrational excitation process. The electron-molecule interaction in the outer region was extracted from the work of Le Dourneuf, Vo Ky Lan, and Launay[32] and joined to a polarization potential.

### B. CAM collision equations

The two interactions present in the CAM approach have very different symmetries: spherical for the electron-molecule part and invariant by translation in a plane parallel to the metal surface for the electron-surface part. We use an approach that favors the molecular part, i.e., we describe the electron-scattering wave function (in the ERT outer region $r \ge r_c$) by an expansion over spherical harmonics $Y_{lm}$ centered on the molecule, associated with an expansion over vibrational levels:

$$\Psi=\sum_{v}\sum_{l,m}\frac{1}{r}F^{v}_{lm}(r)Y_{lm}\chi_{v}(R)\,, \tag{3}$$

where $F^{v}_{lm}(r)$ is the scattering electron radial wave function for the $l,m$ angular mode and $\chi_v(R)$ is the target molecule vibrational wave function.

In the present study, we take the molecular axis perpendicular to the surface, so that the system is invariant by rotation around this axis. As a consequence, $m$ is a good quantum number and expansion (3) contains only the $m$ term corresponding to the $N_2^-$ $^2\Pi_g$ symmetry, i.e., $m=+1$ ($m=-1$ is identical). The case of different molecule-surface orientations has been studied for the fixed nuclei situation by the CAM method.[33]

When expansion (3) is brought into the Schrödinger equation, it yields the following set of coupled equations:

$$-\frac{1}{2}\frac{d^{2}F^{v}_{lm}}{dr^{2}}+V^{\rm ext}_{lm}(r)F^{v}_{lm}+\sum_{l'}\langle lm|V_S|l'm\rangle F^{v}_{l'm}=EF^{v}_{l'm}\,. \tag{4}$$

The radial wave functions are coupled inside each block $v$ by the potential terms and are coupled via the boundary condition (2). The latter leads to the following expression for the resonant mode $Y_{21}$:

$$\left.\frac{d}{dr}F^{v}_{21}(r)\right|_{r=r_c}=\sum_{v'}\langle\chi_v|f_{21}(R)|\chi_{v'}\rangle F^{v'}_{21}(r_c)\,, \tag{5}$$

and, for the nonresonant modes

$$\left.\frac{d}{dr}F^{v}_{lm}(r)\right|_{r=r_c}=f_{lm}F^{v}_{\rm lm}(r_c)\,. \tag{6}$$

The set of equations (4) is solved using a Fox-Goodwin integrator.[34] It is noteworthy that this treatment of vibrational excitation parallels the ERT treatment for electron-free molecule collisions; the extension to physisorbed molecules is made via the $V_S$ coupling terms in Eq. (4).

Equation (4) remains coupled when the electron-molecule distance $r$ goes to infinity. Thus we have to perform a basis change from the $Y_{lm}$ basis to the adiabatic basis $a_{nm}$ that diagonalizes the potential terms at large $r$, and the $S$ matrix is then extracted in this adiabatic angular basis (see discussion in Ref. 17). The $S$-matrix elements are noted as $S_{n_iv_in_fv_f}$, where $v_i$ and $v_f$ refer to the initial and final vibrational levels and $n_i$ and $n_f$ to the adiabatic angular modes ($m$ being a constant has been omitted). By comparison to the case of collisions with a free molecule, we define the inelasticity $I_{v_iv_f}$ for the $v_i\rightarrow v_f$ vibrational excitation:

$$I_{v_iv_f}=\sum_{n_i,n_f}|S_{n_iv_in_fv_f}|^{2}\,. \tag{7}$$

For free molecules, the inelasticity is proportional to the total excitation cross section; this is not the case for adsorbed molecules, since the various $a_{nm}$ angular modes are not degenerate (they correspond to metal and vacuum modes).

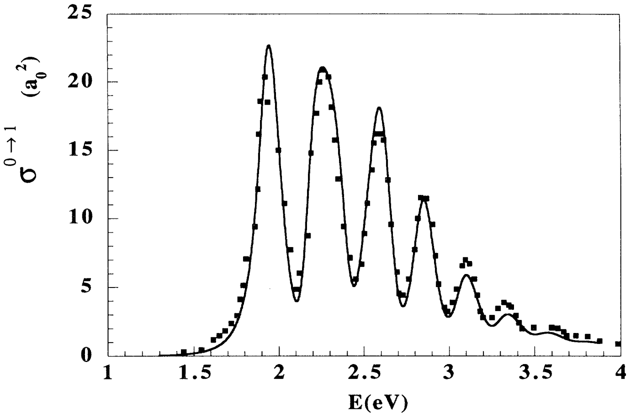

FIG. 1. Total cross section for $v=0\rightarrow v=1$ vibrational excitation of the free $N_2$ molecule by electron impact. Full line: present results. Black squares: experimental results from Wong (Ref. 35).

### C. Vibrational excitation of free molecules

We can check the validity of our ERT modeling of the $e^-$-$N_2$ interaction by computing the vibrational excitation cross section for the free molecule with the above formalism. The total cross section is then given by

$$\sigma^{\rm free}_{\rm Tot}(v_i\rightarrow v_f)=2\frac{\pi}{k^{2}}I_{v_iv_f}\,, \tag{8}$$

where $k$ is the incident momentum of the electron.

Figure 1 presents this total cross section for the 0→1 vibrational excitation as a function of the incident energy, compared with the absolute experimental results of Wong.[35] For the comparison, we assumed that the angular dependence of the cross section was that of a pure $d\pi$ wave, and thus we transformed the differential absolute cross section of Wong into an absolute total cross section. The agreement is quite satisfactory; in particular, the boomerang oscillations with peaks of different widths are rather well reproduced. Similar agreement is obtained for the excitation of the higher-lying $v$ levels. This agreement is not surprising since the ERT boundary condition has been extracted from the work of Dubé and Herzenberg[25] (see above), which was in quite good agreement with experiment. The comparison of Fig. 1 thus gives confidence in the representation of the $e^-$-$N_2$ interaction.

### D. Angular sharing for adsorbed molecules

The $S$ matrix obtained by solving (4) should in principle yield the information required to obtain differential cross sections. However, as explained above, the CAM method makes use of expansion (3) which is well adapted to treat the molecular terms and not the surface terms; as a result, all quantities which depend mainly on the molecular terms are well described with a small number of $l$ in (3), whereas quantities very influenced by the surface terms, such as the angular distributions, require a very large number of $l$ terms. Indeed, after the electron is ejected by the molecule, it is scattered in the $e^-$-surface potential out to infinity, and this is difficult to describe with $Y_{lm}$ functions. In addition, even at large $r$, close to the surface there always exists a region where the forces acting on the electron are large, and this region is also hard to describe. For these reasons, we did not compute differential cross sections but rather what we called *summed cross sections,* which are a generalization of total cross sections to the case of nonisotropic environment. Indeed, there exist two different channels for an electron with different energies: the vacuum and the metal. We define summed cross sections as the integral of the differential cross section over the exit angle, averaged over the incident angle, the two integration domains being restricted to either the metal or vacuum sides. We thus define a $\sigma_{\text{VV}}$ summed cross section which corresponds to collisions in which the electron comes from the vacuum and is ejected toward the vacuum; these are the usual scattering experiment conditions. $\sigma_{\text{VM}}$ corresponds to electrons incident from the vacuum and scattered into the metal; although present in a scattering experiment, this process is not observed. $\sigma_{\text{MV}}$ and $\sigma_{\text{MM}}$ correspond to electrons arriving from the metal side and scattered into the vacuum (metal) side. These correspond to experiments with photoelectrons or hot electrons. The computation of $\sigma_{\text{AB}}$ ($A,B \equiv V$ or $M$) requires the definition of the sharing between the vacuum and the metal sides. We did this by two different methods.

In the first method, we use the solutions of (4) directly. The $S$-matrix elements are extracted in the basis of adiabatic angular modes. For an even number of $l$ terms ($l_M=2$ L),there can be separated in two groups (see in 17): $L$ modes with energies at infinity close to zero and angular distributions mainly pointing toward the vacuum, and $L$ modes with energies at infinite close to $-V_0$ (the bottom of the potential well inside the metal) and angular distributions mainly pointing toward the metal. They could then be called vacuum and metal modes. For an odd number of $l$ ($l_M=2L+1$), there is an additional mode close to $-V_0/2$ pointing toward the surface region and called a surface mode. However, a closer analysis of the modes shows that, among the vacuum modes, the lowest in energy has an energy different from zero (typically a few tenths of an eV) and an angular distribution mainly pointing in the surface region. If one remembers that even at large $r$, there are strong forces in this region pulling the electron toward the metal, then one can assume that the entire population of that mode at finite $r$ will end up in the metal. For the summed cross sections, we thus define the vacuum modes as those with an asymptotic energy close to zero, except the last one; all other modes will be the metal modes. This yields a definition of the sharing:

$$\sigma_{\text{VV}}(v_i \to v_f)=2\pi \sum_{n_i,n_f \in V} \frac{1}{k_i^2}|S_{n_i v_i n_f v_f}|^2 , \tag{9a}$$

$$\sigma_{\text{VM}}(v_i \to v_f)=2\pi \sum_{n_i \in V,n_f \in M} \frac{1}{k_i^2}|S_{n_i v_i n_f v_f}|^2 , \tag{9b}$$

$$\sigma_{\text{MV}}(v_i \to v_f)=2\pi \sum_{n_i \in M,n_f \in V} \frac{1}{k_i^2}|S_{n_i v_i n_f v_f}|^2 , \tag{9c}$$

$$\sigma_{\text{MM}}(v_i \to v_f)=2\pi \sum_{n_i \in M,n_f \in M} \frac{1}{k_i^2}|S_{n_i v_i n_f v_f}|^2 , \tag{9d}$$

where $k_i^2/2$ is the electron energy in the $n_i v_i$ channel.

We also used another definition of the VM sharing based on a classical sharing. If we assume that the strength of the vibrational excitation is determined close to the molecule, then we can define $\sigma_{AB}$ as a product of the inelasticity by an angular sharing term simply defined by the electron scattering in the $e^-$surface potential. This was done by assuming that the electron is ejected according to a $d\pi$ wave, and then scattered in the image charge potential. This leads to the definition of the classical limit angle:

$$\theta_1=\sin^{-1}\left[\left[\frac{4ZE}{4ZE+1}\right]^{1/2}\right] , \tag{10}$$

where $E$ is the asymptotic energy of the electron in the vacuum, and $Z$ is the molecule-surface distance measured from the image reference plane.

If $\theta>\theta_1$, the electron ends up in the metal. One can then define angular factors $g_V$ and $g_M$, which gives the probability for an electron to go into the vacuum (or metal):

$$g_V(E,Z)=2\pi\int_0^{\theta_1}|Y_{21}|^2 \sin\theta\, d\theta \tag{11}$$

and

$$g_M=1-g_V . \tag{12}$$

With this, we can define the summed cross sections:

$$\sigma_{\text{VV}}(v_i \to v_f)=\frac{2\pi}{k_i^2} I_{v_i v_f} g_V(E_i,Z) g_V(E_f,Z) , \tag{13a}$$

$$\sigma_{\text{VM}}(v_i \to v_f)=\frac{2\pi}{k_i^2} I_{v_i v_f} g_V(E_i,Z) g_M(E_f,Z) , \tag{13b}$$

$$\sigma_{\text{MV}}(v_i \to v_f)=\frac{2\pi}{k_i^2} I_{v_i v_f} g_M(E_i,Z) g_V(E_f,Z) , \tag{13c}$$

$$\sigma_{\text{MM}}(v_i \to v_f)=\frac{2\pi}{k_i^2} I_{v_i v_f} g_M(E_i,Z) g_M(E_f,Z) , \tag{13d}$$

where $k_i^2/2$ is the asymptotic energy of the electron in the incident channel.

Figure 2 presents a comparison of the predictions for the summed cross sections by formulas (9) and (13). It displays the $\sigma_{\text{VV}}$ and $\sigma_{\text{VM}}$ cross sections as a function of the incident electron energy for a molecule surface distance of $5a_0$. It is noteworthy that the computation with formulas (9) using the adiabatic angular modes to define the sharing requires a larger number of $l$ terms to reach convergence; the results presented in Fig. 2 were obtained with 17 angular modes for formulas (9) and only seven angular modes for formulas (13). The agreement between the two methods is quite satisfactory. However, large discrepancies can be seen close to threshold in $\sigma_{\text{VV}}$, especially for large $v_f$ excitations. This is due to a defect in the threshold definition in formulas (9). Indeed, in (9), the thresholds are defined with respect to the adiabatic

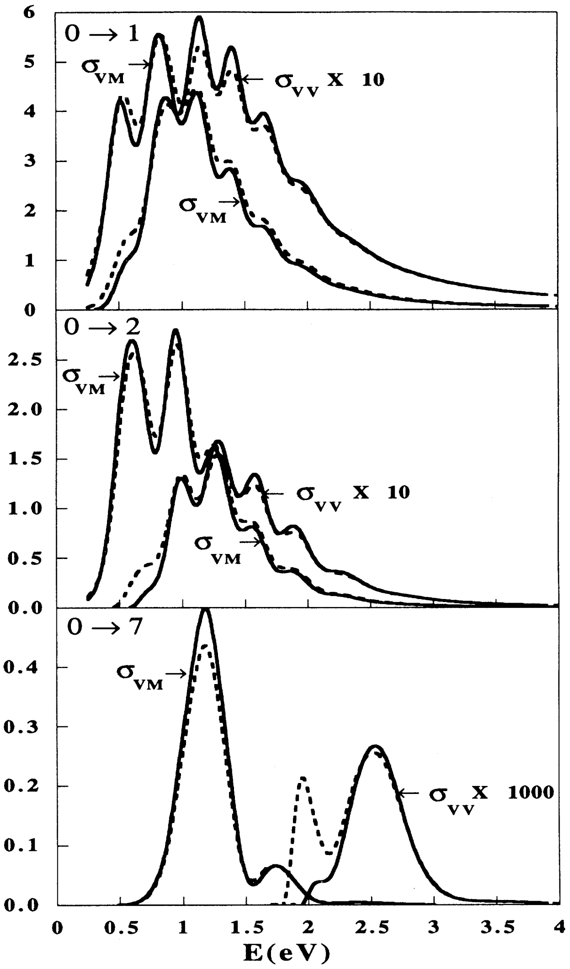

FIG. 2. Comparison between the summed cross sections compared with formulas (9) (dashed lines) and (13) (full lines) as functions of the incident electron energy. The three figures display the cross sections for $v=0 \to v=1$, 2, and 7 excitations for the VV and VM processes (see text for definition).

modes asymptotic energies, which are not exactly zero for the vacuum modes. As a result, the thresholds are moved to energies lower than the real ones. On the contrary, with formulas (13) the thresholds are located at the right energies.

In the following, we use formulas (13), which require a smaller number of $l$ terms in (3) to reach convergence and then a smaller amount of computer time.

## III. RESULTS AND DISCUSSIONS

### A. Inelasticities

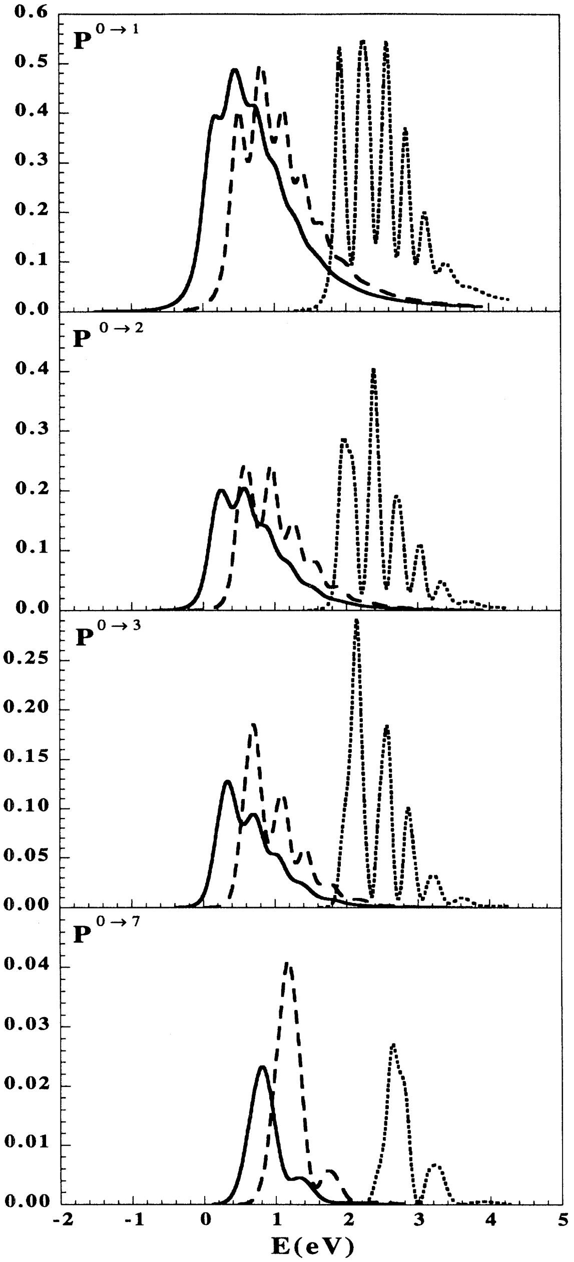

FIG. 3. Inelasticities [defined by formula (7) in the text] for resonant vibrational excitation of a $N_2$ molecule physisorbed on Ag. The four figures present the results for the $v=0 \to v=1$, 2, 3, and 7 excitations as functions of the incident electron energy. Dotted line: inelasticities for the free molecules. Dashed line: inelasticity for a molecule-surface distance of $5a_0$. Full line: inelasticity for a molecule-surface distance of $4a_0$.

Figure 3 presents results for the inelasticities [definition (7)] for the $0\to 1$, $0\to 2$, $0\to 3$ and $0\to 7$ transitions as functions of the electron incident energies. The converged inelasticities can be computed with a rather moderate number of $l$ values ($l_M=7$ in the present case). They have been computed at two different molecule-surface distances ($Z=4a_0$ and $5a_0$) and are compared with those of the free molecule. The computation of inelasticities at different $Z$ values allows us to illustrate the modifications of the vibrational excitation process introduced by the neighboring surface; indeed, in the real $N_2$/Ag surface, the molecule is located at a well-defined $Z$ distance. As the main modifications induced by the metal surface, one can mention the following.

(i) The energy region where the inelasticity differs from zero shifts to lower energy when the molecule approaches the surface. This is connected with the fact that the energy position of the $N_2^-$ ($^2\Pi_g$) resonance moves to lower energies when $Z$ decreases, as found in the previous static studies.[15,16]

(ii) The boomerang oscillations that are pronounced in the case of the free molecule are damped in the case of adsorbed molecules and almost disappear for the smallest $Z$ distances. The boomerang oscillations come from the fact that the intermediate $N_2^-$ molecular ion can perform roughly one vibration during the resonance lifetime. The damping of these oscillations comes from the shortening of the resonance lifetime, found in the previous static studies.[15,16] It is noteworthy that a significant change in the boomerang structure can be obtained by a rather moderate change in the resonance width (40% increase for $Z=5a_0$ compared to the free molecule[36]) at the $N_2$ equilibrium distance. However, one must remember that the molecule vibrates during the collision and experiences regions of internuclear distances $R$ where the width is quite different. In particular, the change is much more important at large $R$, where the resonance energy is lower; as an example, for $R$ distances, where the $N_2^-\ ^2\Pi_g$ energy lies below the $N_2$ energy, the width is not vanishing for an adsorbed molecule, whereas it would for a free molecule (see the discussion in Ref. 36).

(iii) The magnitude of the inelasticity does not vary much with the molecule-surface distance. This can seem surprising at first sight, since the increase of the resonance width mentioned above should result in a decrease of the resonance efficiency for vibrational excitation. However, the width variation only gives a partial view of the problem. Indeed, when the $N_2$ molecule is sitting on a metal surface, the energetics of the vibrational excitation are much modified. For the VV process the energetics are the same as those of the free molecule. However, the processes by which the outgoing electron goes into the metal do not present any energy threshold (the electron gains a kinetic energy equal to $U_0$ when going from the vacuum into the metal). As a result, there is no energy threshold for the VM and MM processes in the few-eV range, and that strongly favors the vibrational excitation. As an example, some of the inelasticities in Fig. 3 are nonzero for negative energies (the energy is referred to the vacuum channel). Thus the variation of the inelasticity with $Z$ is the result of two opposite effects (the increase of the width and the partial disappearance of energy thresholds) which, from Fig. 3, appear to be roughly balanced in the present case. Indeed, for a resonance located at a higher energy, the width effect would most likely dominate.

### B. Summed vibrational excitation cross sections in a scattering experiment

Figure 4 presents the summed vibrational excitation cross sections for a scattering experiment (VV process), for various excitations ($v=0\rightarrow v=1$, 2, 3, and 7) and various molecule-surface distances ($Z=4a_0$, $5a_0$, and $7a_0$) together with the results for the free molecule. For the comparison, the total cross section for the free molecule has been divided by 4 to correspond to a VV process (for a free molecule, the $g$ factors [Eqs. (11) and (12)] are equal to 0.5). Indeed the $\sigma_{VV}$ summed cross sections display features similar to the inelasticities: the energy

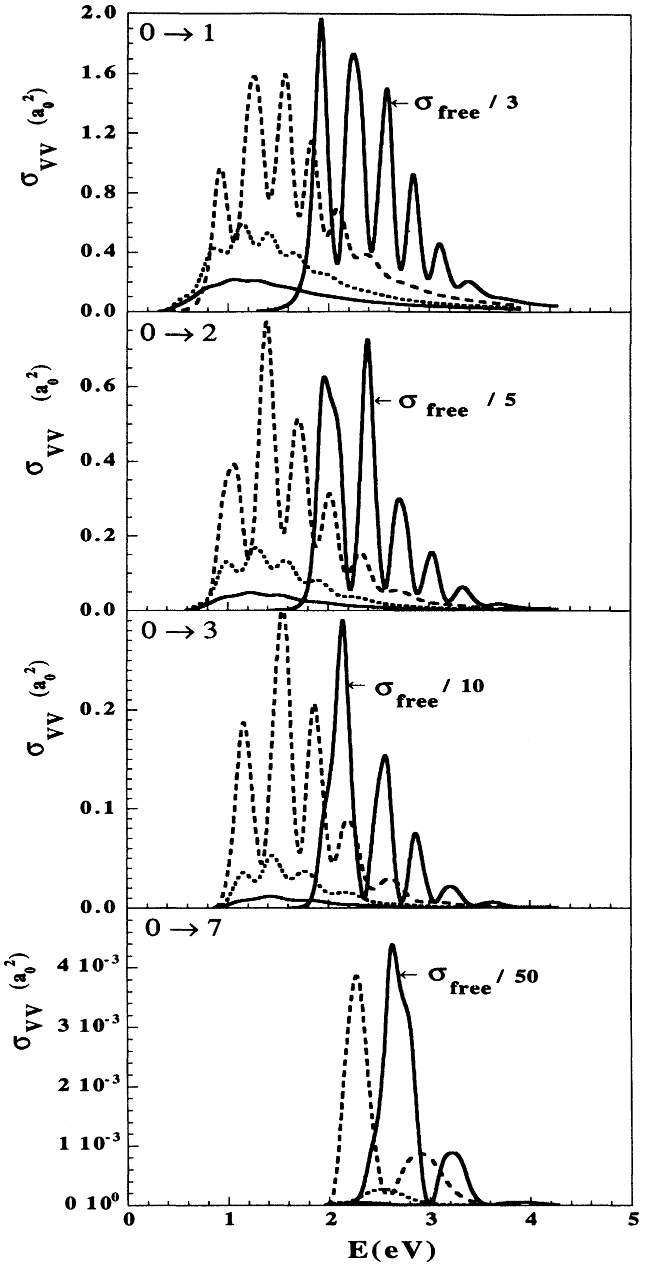

FIG. 4. Summed cross sections $\sigma_{VV}$ for vibrational excitation of $N_2$ in the VV process (see text for definition) as functions of the incident electron energy. The four figures present the $v=0\rightarrow v=1$, 2, 3, and 7 excitations. Full line with label: $\sigma_{VV}$ for the free molecule (it is defined as the total excitation cross section divided by 4). Dashed line: $\sigma_{VV}$ for a molecule-surface distance of $7a_0$; dotted line: $\sigma_{VV}$ for a molecule-surface distance of $5a_0$; full line (unlabeled): $\sigma_{VV}$ for a molecule-surface distance of $4a_0$.

domain of the resonant excitation shifts to smaller energies, and the oscillations disappear when the molecule-surface distance decreases. The situation for the magnitude of the $\sigma_{VV}$ cross section is quite different from that of the inelasticity: the cross section decreases when $Z$ decreases, and the effect is much stronger for the high-$v$ excitations than for the lower ones. Comparing Figs. 3 and 4, one can conclude that this decrease of the $\sigma_{VV}$ cross sections is due to a change in the VM sharing. In Sec. III A, among the two effects discussed which influence the inelasticity magnitude (change of the width, change of energetics), one of them (change of energetics) concerns only the $M$ side and so cannot influence $\sigma_{VV}$, which then decreases with decreasing $Z$. One can notice that this decrease is stronger the larger the vibrational quantum number change in the process. This is particularly visible on the $v=0 \rightarrow v=7$ cross sections, which also are seen not to shift in energy with $Z$. This is again linked to a threshold effect. The threshold for the $0 \rightarrow 7$ excitation is at 1.95 eV. In the free molecule, the resonance position for the $N_2$ equilibrium distance is 2.3 eV, slightly above the $0 \rightarrow 7$ threshold. Even with the effect of the threshold law, which reduces the cross section close to threshold, the $\sigma_{VV}(0 \rightarrow 7)$ can maximize around the resonance position in that case. However, for smaller $Z$, the resonance moves to energies much below the threshold for $v=7$, excitation and the $\sigma_{VV}(0 \rightarrow 7)$ cannot maximize at the resonance position; it does not move down in energy and is blocked somewhere slightly above its threshold. As another consequence, $\sigma_{VV}(0 \rightarrow 7)$ at small $Z$, which can only exist in the far wing of the resonance, is very weak. The absence of shift with $Z$ of the $\sigma_{VV}(0 \rightarrow 7)$ cross section is then directly connected with its smallness.

### C. Comparison between the VV and VM processes

Figure 5 presents a comparison between the summed cross sections for the VV and VM processes at a molecule-surface distance of $5a_0$. As a general feature, the $\sigma_{VM}$ cross section is much larger than the $\sigma_{VV}$ one, and the difference is larger at small collision energies and for large $v$ excitations. This comes from the very same energetics effect discussed above. When the energy of the electron is small in the final-state channel, it is very sensitive to the attraction by the image charge potential. Then only a small fraction of the electrons scattered in this channel will eventually escape toward vacuum, most of them going into the metal. This accounts for the large difference between VV and VM. At higher collision energies, the electron is less sensitive to the image charge potential, and the $\sigma_{VM}/\sigma_{VV}$ ratio goes to 1. The threshold effect is well illustrated by the $(0 \rightarrow 7)$ excitation. The $\sigma_{VV}$ cross section is small and exists only above its threshold ($E=1.95$ eV); in contrast, the $\sigma_{VM}$ cross section can maximize at much smaller energies around the resonance position and is thus much larger. Comparing Figs. 5 and 4 also shows that the $\sigma_{VM}$ summed cross sections for $Z=5a_0$ are roughly of the same order of magnitude as their equivalents for the free molecule.

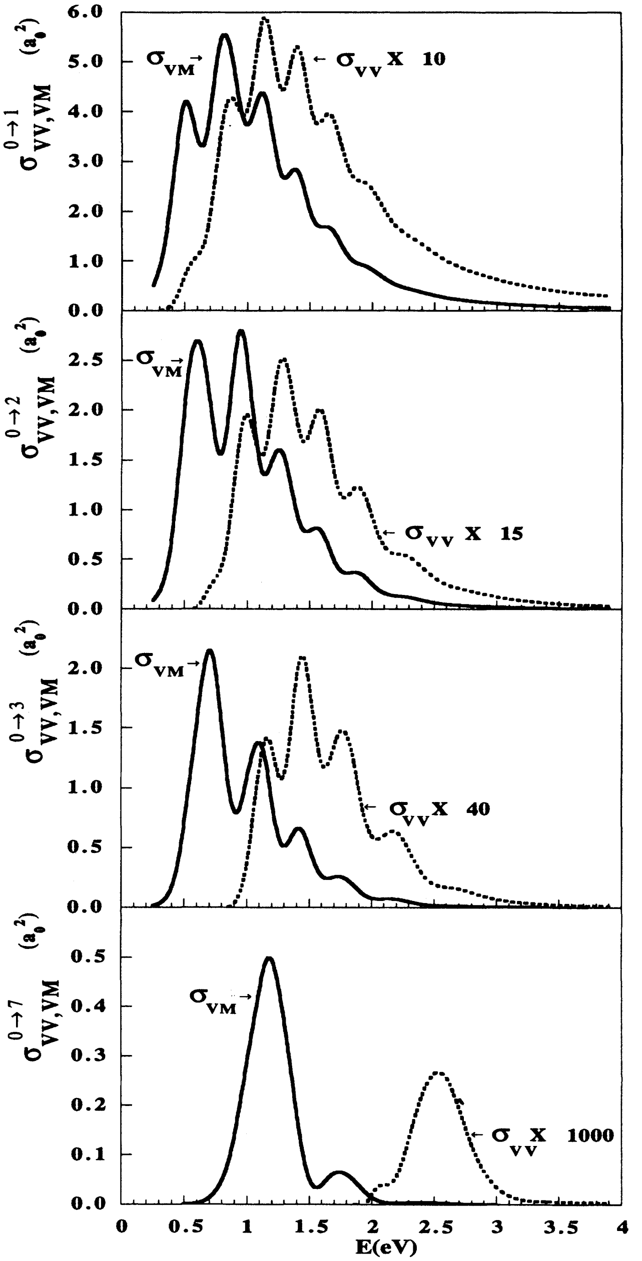

FIG. 5. Comparison between the summed cross sections for the VV (dotted lines) and VM processes (full lines) as functions of the incident electron energy (note the multiplicative factor for the $\sigma_{VV}$ cross sections). The four figures display the results for the $v=0 \rightarrow v=1$, 2, 3, and 7 excitations.

Figure 6 presents a comparison between the summed $\sigma_{VV}(0 \rightarrow 1)$ and $\sigma_{VM}(0 \rightarrow 1)$ cross sections for various molecule-surface distances $Z$ (the two cross sections are equal in the limit $Z \rightarrow \infty$). As expected, the difference between the two cross sections increases as $Z$ decreases. In particular, at $Z=4a_0$, the energy shift between the two cross sections is quite sizable: the resonance position is now rather low (0.5 eV for the $N_2$ molecule equilibrium distance[15]) in a region rather close to the $(v=0 \rightarrow v=1)$ excitation threshold for the VV process, and then the

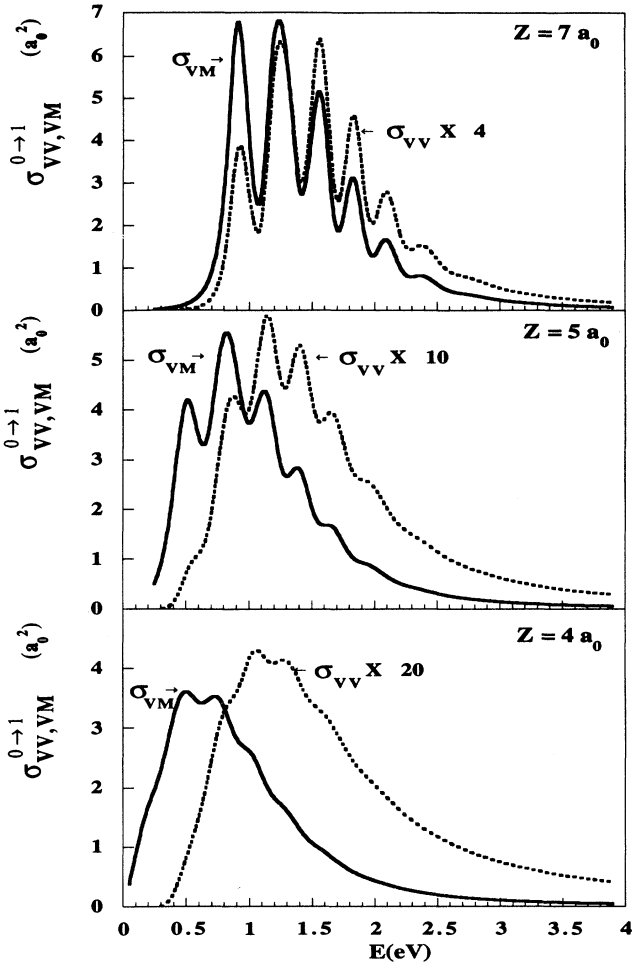

FIG. 6. Comparison between the summed cross sections for $v=0\rightarrow v=1$ excitation for the VV (dotted lines) and VM processes (full lines) as functions of the incident electron energy for three different molecule-surface distances: $Z=4a_0$, $5a_0$, and $7a_0$ (note the multiplicative factor for the $\sigma_{VV}$ cross sections).

$\sigma_{VV}(0\rightarrow1)$ cross section maximum appears to shift from the resonance position.

These results for VV and VM processes somewhat modify what is known from scattering experiments on the vibrational excitation of adsorbed molecules. In the present case, it appears that when estimating the importance of the vibrational excitation from a scattering experiment, one misses most of the process; indeed for $v=1$ excitation, 90% of the excitation is in the VM process and is not observed in a scattering experiment. For the $v=7$ excitation, a scattering experiment only looks at a $5\times10^{-4}$ fraction of the total excitation. The resonant vibrational excitation of adsorbed molecules is then much more important than expected, and this should be taken into account when considering energy deposition on surfaces. It is noteworthy that this result is influenced by the choice of Jenning's potential (1) to describe the electron-surface interaction; another choice of interaction, in particular including the effect of the surface cristallography, could lead to different surface reflectivity and hence to different results. Rous[18] has shown in a static study (computation of the position and width of the molecular resonance) that the cristallographic structure can play a role; however, he did not find any effect for the $N_2$/Ag case. Nevertheless, one can stress that the effect discussed above is mainly an *energy* effect, and it will be present with any surface reflectivity. For example, the large difference between VV and VM for the $0\rightarrow7$ excitation (Fig. 5) is due to the fact that the resonance is below the VV threshold and is independent of the surface reflectivity.

### D. Overtone excitation

The variation in the excitation of the high vibrational levels that can be seen in the previous figures can be summarized by looking at the overtone excitation ratios. These are rather important quantities, since high overtone excitation is usually recognized as a signature of a resonant process. Various definitions can be used for the overtone excitation ratio. In Fig. 7, we present the ratio between the summed cross section for the excitation of the $v$ level to that for the $v=1$ level, both cross sections being taken at their maximum. Figure 7(a) presents the results for the free molecule compared to those for the VV and VM processes at a molecule-surface distance of $5a_0$. The overtone excitation is found to be much weaker for the VV process than it is for the VM process or for

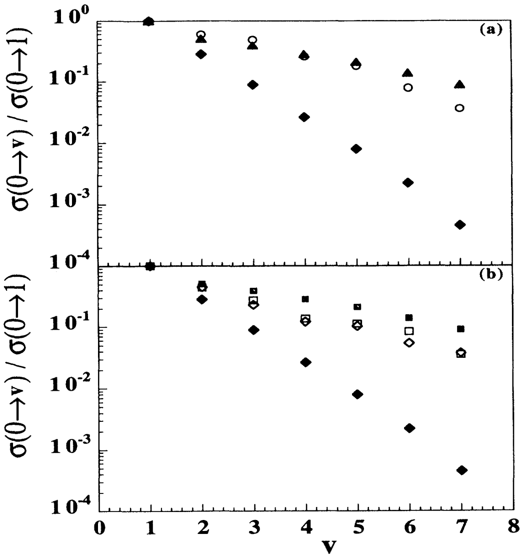

FIG. 7. Overtone excitation ratios for the resonant vibrational excitation of $N_2$. The overtone ratio is defined as the ratio between the $0\rightarrow v$ excitation cross section to that of the $0\rightarrow1$ excitation, taken at their maxima. (a) Comparison between the various processes: free $N_2$ molecule (open circles), VM process (black triangles), and VV process (black diamonds) for a physisorbed $N_2$ molecule (molecule-surface distance $Z=5a_0$). (b) Comparison with a model test calculation (see text): black symbols VV (diamonds), VM (squares), open symbols are the results of the test calculation (VV: diamonds; VM: squares).

the free molecule. One again notices a very large underestimation of the vibrational excitation efficiency if one considers only the process which is observed in a scattering experiment.

It is quite remarkable that the overtone excitation in the VM process is roughly equal to that of the free molecule; i.e., upon adsorption, although the resonance width is increased, which should result in a significant decrease of the overtone excitation, the VM process keeps its efficiency whereas the VV process does not. This is again due to the fact that the width is not the only active parameter for this problem: there is also an energy effect: the energetics of the VM process are different from that of the free molecule. This interpretation was checked by performing a vibrational excitation study on a fake molecule which has all the $N_2$ properties except that the $v$ levels are degenerate. This deeply modifies the energetics of the VV process; it should favor vibrational excitation, which then does not require any energy transfer and does not have any energy threshold. Figure 7(b) presents the results of this test calculation: the high-$v$ excitation in the VV process is much increased compared to the real case, and the VV and VM processes have roughly the same efficiency. The variation of the VV overtone excitation between Figs. 7(a) and 7(b) confirms the interpretation in terms of an energy effect. The almost equality between the VM case and the free molecule [Fig. 7(a)] then appears as an almost exact balance between two opposite effects: the width increase and the threshold disappearance effect.

### E. Vibrational excitation by "metal electrons" (MM and VM processes)

Figure 8 presents the vibrational excitation summed cross sections for the MM and MV processes (molecule-surface distance equal to $5a_0$). They correspond to electrons coming from the metal i.e., to an experimental situation of photoelectrons or hot electrons interacting with an adsorbed layer. Here again, the efficiency of vibrational excitation is rather high. The results are presented in terms of scattering cross sections [Eqs. (13c) and (13d)], although they do not correspond to a scattering experiment. It is noticeable that the MM cross sections are roughly of the same order of magnitude as the VM cross sections, although the incident energy entering in the cross-section expressions are quite different [Eq. (13)]; the MM process is then associated with quite substantial vibrational excitation probabilities. The discussion of Fig. 8 closely follows that of Fig. 5. In particular, one can notice that the difference between VV and VM processes is identical to that between MM and MV processes.

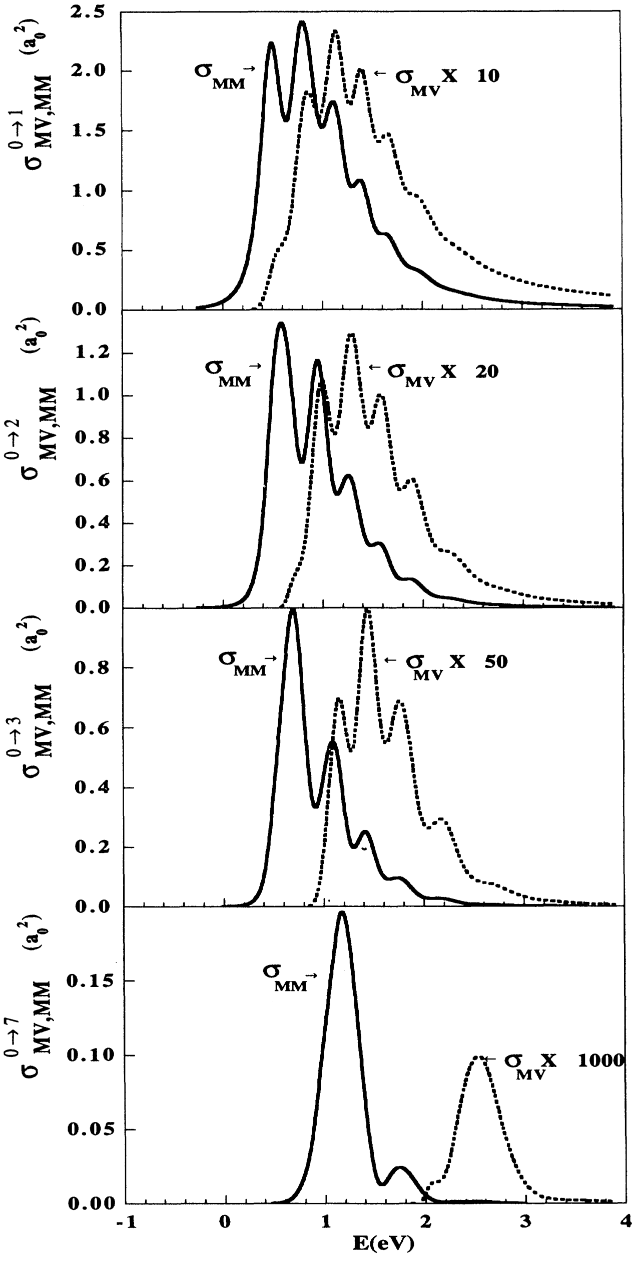

FIG. 8. Summed cross sections for vibrational excitation of physisorbed molecules by electrons coming from the metal: full line: MM process; dotted line: MV process. The horizontal scale is the incident electron energy measured with respect to the vacuum level. The molecule-surface distance is $Z=5a_0$. The four figures display the results for the $v=0\to v=1$, 2, 3, and 7 excitations.

### F. Comparison with experiments

The above theoretical results of the VV process can be compared with the experimental results of Demuth, Schmeisser, and Avouris[3] and Schmeisser, Demuth, and Avouris[14] who studied the vibrational excitation in a scattering experiment. They reported on the relative vibrational excitation cross section ($v=0\to v=1$) as a function of the incident electron energy, for a given incident and a given scattering angle. Since the vibrational excitation has a resonant character, one can expect the angular distribution of scattered electrons to be characteristic of the resonance and then not to vary much with the electron energy. One can also mention that the experiments were performed with a polycristalline Ag tar-

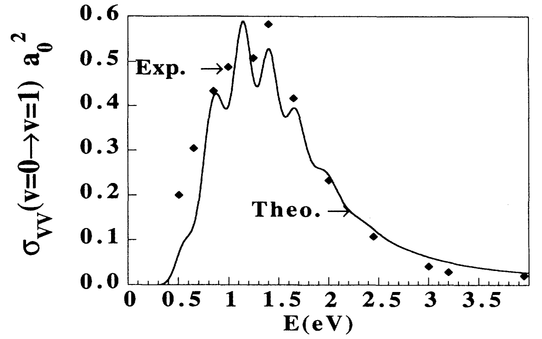

FIG. 9. Comparison of the present results for the summed cross sections for the $v=0\rightarrow v=1$ excitation, VV process (full line) with the experimental results of Demuth, Schmeisser, and Avouris (Ref. 3) (black diamonds) as functions of the incident electron energy. The absolute vertical scale corresponds to the present results, and the experimental results have been scaled to them.

get, and that this should also introduce some averaging in the angular distribution. One can then compare the energy dependence of our summed cross section (VV process) with that of the differential results of Demuth, Schmeisser, and Avouris.[3] Figure 9 presents this comparison. The agreement is quite satisfactory; in particular, there is a good agreement between the two shapes. The theoretical results of Fig. 9 were obtained for a molecule-surface distance of $5a_0$. This distance corresponds to the range of $Z$ distances where the theoretical position of the cross section agrees with experiment. It is noteworthy that this distance corresponds to the value of the adsorption distance one can obtain from the study of molecule-surface scattering by Corey and Alexander.[37]

Figure 10 presents a comparison between the present results and the experimental results of Schmeisser, Demuth, and Avouris[14] for the overtone excitation ratio. The experimental overtone ratio was defined as the ratio of the peaks in the high-resolution electron-energy-loss spectroscopy (HREELS) spectrum for an incident electron energy of 1.5 eV. Two theoretical definitions (VV process) appear in Fig. 10: the first with a ratio of the summed cross sections at their maximum (same as in Fig. 7), and the second with a ratio of the summed cross sections at an incident energy of 1.5 eV (this ratio only exists for $v\leq 5$). The two definitions lead to very similar values, except for the $v=5$ point which is very close to the threshold at $E=1.5$ eV and is thus very small and very sensitive to inaccuracies in the energy definition. The agreement between theory and experiment is quite satisfying, and once again confirms the validity of the present description of the resonant vibrational excitation process.

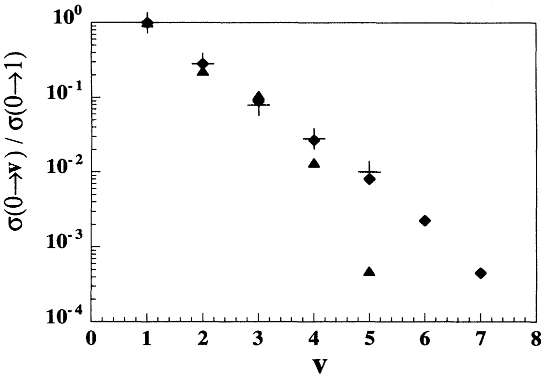

FIG. 10. Comparison of the present results for the overtone excitation ratio with the experimental results of Demuth, Schmeisser, and Avouris (Ref. 3) and Schmeisser, Demuth, and Avouris (Ref. 14). Two definitions have been used for the theoretical overtone ratios: the black diamonds are obtained as ratios between the excitation cross sections (VV process) taken at their maxima, and the black triangles are obtained as ratios between the excitation cross sections (VV process) at a fixed energy (1.5 eV). The molecule-surface distance is $Z=5a_0$.

Vibrational excitation of $N_2$ molecules physisorbed on Al(111) was studied by Jacobi *et al.*[38] They reported on a vibrational excitation cross section ($v=0\rightarrow v=1$) that peaks around 1.4 eV with a width of 1.4 eV; these results are quite comparable to those of Demuth, Schmeisser, and Avouris[3] and the present theoretical ones (Fig. 9). The slightly larger value of the maximum position for the cross section might be an indication of a larger adsorption distance for Al(111). Sanche and Michaud[39,40] have also studied vibrational excitation of $N_2$. In particular, they worked on $N_2$ molecules on Pt surfaces with a spacer layer of Ar of variable thickness between $N_2$ and Pt. Their results for the vibrational excitation cross section nicely display the shift to lower energies of the excitation cross section due to the substrate polarization (Ar/Pt). It is noteworthy that for a thin spacer layer and no Ar layer, they found vibrational excitation cross sections much broader in energy (a typical width of 2 eV) than the ones of Fig. 9. This broadening could come from fluctuations in the films and/or the local potentials.[40]

## IV. CONCLUDING SUMMARY

We have presented a theoretical study of vibrational excitation by electron impact of $N_2$ molecules physisorbed on an Ag surface. Describing the metal surface environment by a local potential acting on the collisional electron, we obtained qualitative results for the resonant vibrational excitation process.

As the main results, the ${}^2\Pi_g N_2^-$ resonance, which is known to dominate the low-energy $e^-$-free-$N_2$ scattering, is still very efficient for the physisorbed molecules. The vibrational excitation cross sections for a scattering experiment are found to shift to lower energies, and the boomerang oscillations visible for the free molecule almost disappear for adsorbed molecules. These scattering cross sections are found to be weaker for adsorbed molecules than for the free molecule, and the overtone excitation is substantially decreased. However, in fact, the resonance is still very efficient, but its effects are less visible: in a scattering experiment on adsorbed molecules, vibrational excitation is a strong process with large overtone excitations; however, most of this process results in electrons finally going into the metal. Thus most of the vibrational excitation present in a scattering experiment is not visible. It should be visible through its consequences: reactions induced by the presence of excited species on the surface (desorption, chemical reactions, etc.). Similarly, the vibrational excitation by electrons coming from the metal was found to be important.

The vibrational excitation cross sections in a scattering problem ($\sigma_{VV}$) decrease upon adsorption of the molecule. Earlier, this feature was attributed to the decrease of the resonance lifetime. However, from the present study, it appears that the resonance width is not the only parameter influencing the cross section. The modification of the energetics of the problem also plays an important role: in particular, the absence of an energy threshold for the vibrational excitation and of an energy barrier for the electrons scattered into the metal strongly favors the vibrational excitation and balances the effect of the width variation. These energy effects should be very important for all systems with a low-energy resonance.

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