ELSEVIER

Surface Science 443 (1999) 57–68

surface science

www.elsevier.nl/locate/susc

Vibrational excitation in low-energy electron scattering by H_2 molecules physisorbed on a metal surface

D. Teillet-Billy [a], D.T. Stibbe [b,1], J. Tennyson [b], J.P. Gauyacq [a,*]

[a] *Laboratoire des Collisions Atomiques et Moléculaires, Unité mixte CNRS–Université, UMR 8625, Bâtiment 351, Université Paris-Sud, F-91405 Orsay Cedex, France*

[b] *Department of Physics and Astronomy, University College London, London WC1E 6BT, UK*

Received 4 June 1999; accepted for publication 4 September 1999

Abstract

The electron impact vibrational excitation of H_2 molecules physisorbed on a free-electron metal surface is studied theoretically at collision energies of a few eV. The role of the short-lived low-lying $^2\Sigma_u$ resonance is investigated. The electron scattering by a free H_2 molecule is described by the R-matrix method and the corresponding results are used to model the electron scattering by the physisorbed molecule with the coupled angular mode (CAM) method. The strength of the vibrational excitation and, in particular, the overtone vibrational excitation ratio are found to be smaller for the physisorbed molecule than for the free molecule. However, the energy dependence of the vibrational excitation process is found to be weakly influenced by the physisorption, as observed experimentally by Demuth et al. [Phys. Rev. Lett. 47 (1981) 1166]. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen; Low-energy electron scattering; Physisorption; Vibrational excitation

1. Introduction

The transfer of energy from electronic motion to molecular vibrational motion in the course of an electron–molecule collision is usually inefficient owing to the unfavourable mass ratio between the electron and the nuclei. However, if the electron can be captured by the target molecule to form a transient negative ion, a resonance, the increase in collision time can make this energy transfer much more probable. The resonant vibrational excitation of molecules by electron impact is a well-documented process, both for free molecules and for molecules adsorbed on solid surfaces [1–3]. In the case of a molecule physisorbed on a solid surface, modifications of the electronic structure of the molecule are rather limited and, thus one can expect each resonance in the free molecule to be associated with a resonance of the physisorbed molecule and, vice versa [4,5]. Comparison between the two cases allows analysis of the perturbation of the resonance by the solid surface. In other words, it provides a way of studying how a resonant state of a molecule and, more generally, how the electron scattering properties of the molecule are perturbed by the environment of the molecule. In addition, the adsorption of the molecule introduces new channels into which the molecular resonances can decay:

---

* Corresponding author. Fax: +33-1-69-157-671.

E-mail address: gauyacq@lcam.u-psud.fr (J.P. Gauyacq)

[1] Present address: Laboratoire de Photophysique Moléculaire, Bâtiment 213, Université Paris-Sud, F-91405 Orsay Cedex, France.

PII: S0039-6028(99)00964-4

excitation of the frustrated rotational and translational motions, excitation of the molecule–surface vibrational motion, desorption of neutrals or ions, and reactivity at the surface.

A few theoretical studies have been devoted to the dynamics of these processes, mainly the case of resonant vibrational excitation. In one class of studies, termed 'static' [6–8], the resonance-state characteristics (energy position and lifetime) are determined in the local complex potential approximation [6,9] and can be used for further approximate treatments of the collision dynamics. These studies showed that, compared with the free molecule, the resonance energy decreases and its width increases when the molecule is adsorbed on a free-electron metal. These effects can be easily rationalised by invoking the image charge interaction between the active electron and the metal surface. Most of the above studies involved free-electron metals as substrates; however, it has been shown in static studies that the band structure of the substrate can significantly influence the molecular resonance characteristics, the energy and the width [10]. The target band structure has also been found to have a similar effect on the energy position and width of atomic levels interacting with a metal [11]. However, the energy and the lifetime of the resonance are not the only parameters governing the vibrational excitation process. A dynamical treatment of the vibrational excitation has been developed using the coupled angular mode approach (CAM) [12]. Associated with the effective range theory (ERT) [13] model representation of the electron–molecule interaction, it allows an exact treatment of the electron–vibration energy transfer. These studies [14–16] have revealed the very strong effect of the asymmetry introduced by the surface that splits the space into two regions: vacuum and bulk substrate.

Two molecular resonances of different characteristics have been studied for molecules physisorbed on free-electron metals: (1) the $N_2^-(^2\Pi_g)$ resonance [14,15], which is located at low energy in the few eV range and has a moderate width of the order of magnitude of the N_2 vibrational quantum (the situation of the well-known 'boomerang' model [17]); and (2) the $N_2^-(^2\Sigma_u)$ resonance [16] located at much higher energy in the 20 eV range with a very short lifetime. The dynamic results are quite different in the two cases. The $N_2^-(^2\Pi_g)$ resonance is strongly influenced by the metal surface; its energy and width are modified by the presence of the surface but, most significantly, the asymmetry introduced by the surface is much enhanced by the low energy position of the resonance. The resonance decays mainly by emitting electrons into the metal, so that most of the electrons that are scattered inelastically cannot be observed in a typical electron-scattering experiment. In the case of the high-energy $N_2^-(^2\Sigma_u)$ resonance, the very fast decay (short lifetime) of the resonance is not much changed by the surface. The effect of the vacuum–metal asymmetry is weak due to the high energy of the active electron and so the effect of the metal surface reduces mainly to an energy shift in the vibrational excitation cross-section due to the image charge interaction.

In the present work, we study the case of the $H_2^-(^2\Sigma_u)$ resonance which presents a situation different from the other two resonance: low energy position and extremely short lifetime. We can thus expect an effect of the molecular environment different from that found for the above two N_2^- resonances. The vibrational excitation process due to this resonance has been very well characterised for free molecules [18–23]. At the H_2 equilibrium distance, the $H_2^-(^2\Sigma_u)$ resonance is approximately centred at 0.83 eV with a width of 9.5 eV [24]. However, owing to the large width, these characteristics cannot be determined accurately and they even lose part of their meaning [25]. The $H_2^-(^2\Sigma_u)$ resonance has been observed in the vibrational excitation of H_2 molecules physisorbed on metals [5,26]. The experimental vibrational excitation cross-sections look similar for the free and the physisorbed molecule.

Below, we report on a study of the $H_2^-(^2\Sigma_u)$ resonance for H_2 physisorbed on a free-electron metal, taken with the characteristics of silver. The dynamics of the vibrational excitation treated within the ERT approximation associated with the CAM treatment. The ERT representation of the electron–H_2 molecule interaction is obtained via a parameterisation of recent *R*-matrix ab initio results [24]. A preliminary study of this problem [27] has been performed with a simplified description of the electron–H_2 interaction and within the energy-modified adiabatic approximation [28] for the vibrational motion. Below, Section 2 presents the method used to treat the electron interaction with a free molecule and with a molecule physisorbed on silver, treated as a free-electron metal. Section 3 is devoted to the results for the vibrational excitation of the H_2 molecule by electron impact via the $H_2^-(^2\Sigma_u)$ resonance and Section 4 makes a few concluding remarks.

2. Method

The present study follows the same lines as the previous studies on electron–N_2 scattering by Djamo et al. [14,15], and so only the general method is presented here, together with the specifics for the H_2 system. The basic idea of treatment of electron scattering by an adsorbed molecule within the CAM procedure is to assume that the interactions of the scattering electron with the molecule and with the surface are additive and do not perturb each other. Such an approximation is justified in the case of a physisorbed molecule, the electronic structure of which is not much modified by the adsorption. It corresponds to the case where there is a single molecule adsorbed on the surface. For the electron–silver surface interaction, we use a free-electron description of the silver metal which retrieves the image potential at large electron–surface distances [29]. For the electron–H_2 interaction, we use an ERT description [13] adjusted to reproduce *R*-matrix ab initio results.

2.1. *R-matrix calculations*

Eigenphase sums for low-energy gas-phase electron–H_2 scattering as a function of H_2 internuclear separation, *R*, were taken from *R*-matrix calculations. These calculations were based on the work of Stibbe and Tennyson [24], who studied H_2 resonances up to 12 eV using the UK molecular *R*-matrix programs [30]. These calculations provided a complete explanation of the complicated, vibrationally resolved resonance structure of H_2 and its isotopomers in this region [31].

Eigenphases for $^2\Sigma_u$ symmetry were obtained by using a close-coupling expansion of seven H_2 target states and an *R*-matrix sphere of $20a_0$. Partial waves with l up to 6 were retained in the expansion, which means that p, f and h wave scattering from the ground state was explicitly allowed for. Further details of the calculation can be found elsewhere [24]. At small *R*, it is not possible to detect the low-energy shape resonance in the eigenphase sums. However, the resonance feature becomes increasingly prominent and narrow for *R* greater than the H_2 equilibrium bond length of $1.4a_0$. This behaviour can be seen in the eigenphases shown in Fig. 1. At *R* greater than $2.9a_0$, the resonance crosses the H_2 ground-state potential and becomes a bound state of H_2^-.

2.2. *ERT parameterisation*

The basic idea of the ERT method is to define two regions of space inside and outside the molecule. The system is described by an energy-independent resonance wave function in the inner region and by a vibrational close-coupling expansion with uncoupled angular waves in the outer region. The two descriptions are matched on the boundary (radius r_c). In practice, the description reduces, for each angular mode, to a potential describing the electron–molecule interaction in the outer region and a boundary condition, *f*, independent of the energy, on the radial wave function at $r=r_c$. The external potentials are taken as polarisation potentials with the *R*-dependent polarisability and quadrupole of the H_2 molecule [32] (*R* is the molecule internuclear distance). The boundary condition *f* is a priori a function of the molecule internuclear distance. For each *R* value and each angular mode, it is determined by adjusting the phase shifts computed with the ERT approach to reproduce the *R*-matrix phase shifts for the fixed-*R* problem. Fig. 1 presents the results of this procedure for $^2\Sigma_u$ symmetry of the collision complex: the phase shifts are presented as functions of the collision energy for a few H_2 internuclear distances. In the ERT approach, the $^2\Sigma_u$ symmetry is represented by a pσ angular mode (in the molecular frame). The ERT parameterisation reproduces the low-energy electron scattering rather well. It must be

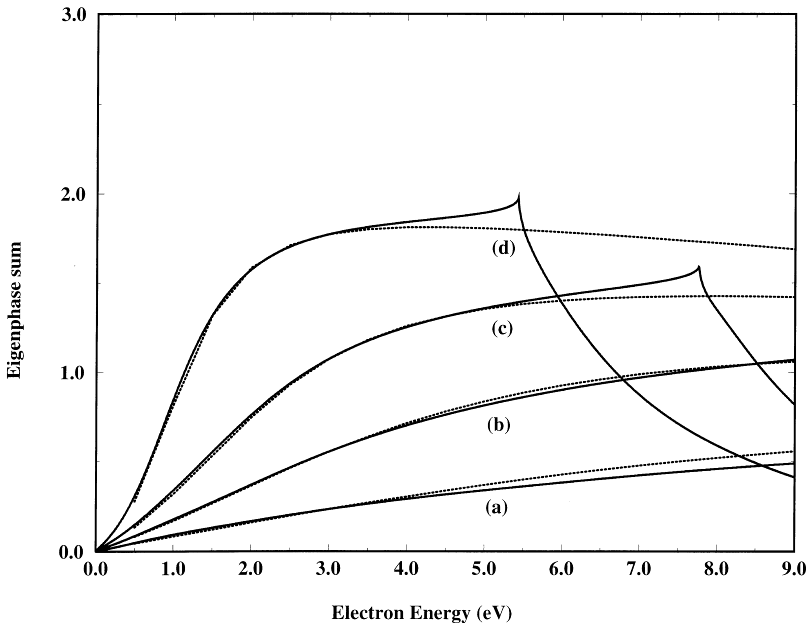

Fig. 1. $^2\Sigma_u$ symmetry electron–H_2 molecule at a fixed internuclear distance, R: eigenphase sum obtained in the R-matrix approach (full lines) compared with the eigenphase shift obtained in ERT modelling (dotted line). The different curves correspond to different internuclear distances: (a) $R=0.802a_0$, (b) $R=1.402a_0$, (c) $R=1.802a_0$ and (d) $R=2.202a_0$.

stressed that only one number is adjusted for each internuclear distance. The phase shifts shown in Fig. 1 display the energy dependence characteristic of a very broad resonance. This is the low-energy $^2\Sigma_u$ resonance that dominates the vibrational excitation process at low collision energies and is the subject of the present study.

At large energy, the R-matrix results show the effect of opening an inelastic electronic channel (the H_2 $b^3\Sigma_u$ channel) that is not present in the ERT phase shifts. The present ERT parameterisation only contains one electronic channel, the H_2 ground state, and is thus limited to low-energy scattering. It is possible to extend the ERT method to higher energies by including other electronic channels and their couplings (see, for example, Refs. [33,34]). In this work, the ERT parameterisation was performed for the $^2\Sigma_u$ and $^2\Sigma_g$ symmetries (pσ and sσ waves, respectively) which are the most important ones for the low-energy vibrational excitation. For the other symmetries, we simply took a boundary condition f corresponding to scattering by a pure polarisation potential.

The vibrational excitation process for the free molecule is described by a close-coupling expansion over spherical harmonics (the electron angular modes) and over $\chi_v(R)$, the vibrational levels of the H_2 molecule:

$$\Psi=\sum_{l,m}\sum_{v} Y_{l,m}\phi^v_{l,m}(r)\chi_v(R)=\sum_{l,m}\psi_{l,m}, \tag{1}$$

where l, m are the spherical harmonics indices and $\phi^v_{l,m}(r)$ are the electron radial wave functions in each channel. This expansion does not take into account the rotational motion of the molecule. The rotation time of H_2 is much longer than the collision time in the present study, so one can consider the orientation of the molecular axis as fixed in space during the collision. The electron radial wave function has to fulfil the ERT boundary condition for the fixed-R problem:

$$\left.\frac{1}{\psi_{l,m}}\frac{\mathrm{d}\psi_{l,m}}{\mathrm{d}r}\right|_{r=r_c}=f_{l,m}(R), \tag{2}$$

where $f_{l,m}(R)$ is the fixed-R boundary condition for the (l, m) angular wave. This expression is integrated over R to yield the boundary condition for the $\phi^{v}_{l,m}(r)$ channel radial wave functions:

$$\left.\frac{\mathrm{d}\phi^{v}_{l,m}}{\mathrm{d}r}\right|_{r=r_c} = \sum_{v'} \phi^{v'}_{l,m}(r_c)\langle\chi_v|f_{l,m}(R)|\chi_{v'}\rangle, \qquad (3)$$

The expansion (1) is substituted into the Schroedinger equation, yielding a set of coupled equations for $\phi^{v}_{l,m}(r)$, the electron radial wave functions, that describe the electron scattered by the vibrating molecule. These equations are only solved in the ERT outer region ($r>r_c$) subject to the boundary condition (3) at r_c. For the free molecule, the (l, m) blocks in the equations are decoupled. The different vibrational channels are coupled by the ERT boundary condition and by the R-dependent polarisation potential. The solution of the coupled equations leads to the scattering S-matrix and to vibrational excitation cross-sections. This procedure corresponds to the exact treatment of the inelastic scattering, within the ERT representation, of the electron–molecule interaction.

The corresponding results for gas-phase electron–H_2 collisions have been calculated for the $(v=0)\rightarrow(v'=1, 2, 3)$ excitations as functions of the energy. Fig. 2 compares these with earlier results, both experimental [18–21] and theoretical [22,23]. The excitation cross-section exhibits the broad energy dependence characteristic of a short-lived resonance. However, the $(v=0)\rightarrow(v'=3)$ excitation cross-section presents a few oscillations that are due to the increase of the resonance lifetime when the molecule stretches (see discussion in Refs. [35,36]). The present results agree reasonably well with the earlier theoretical ones, although the present cross-section is slightly smaller for the $(v=0)\rightarrow(v'=1)$ excitation. This confers confidence in the ability of the present ERT approach to represent the electron–H_2 low-energy interaction.

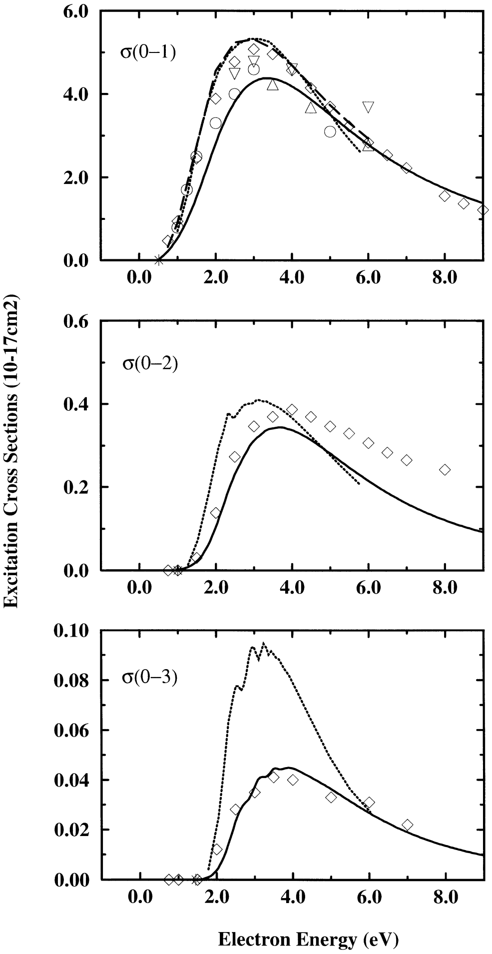

Fig. 2. Vibrational excitation cross-section (in units of 10^{-17} cm^2) of a free H_2 molecule ($^2\Sigma_u$ symmetry) by electron impact as a function of the electron energy. The three panels correspond to the excitation from the $v=0$ vibrational level to the $v'=1$, 2 and 3 levels. Experiments: ◇, Ehrhardt et al. [18]; △, Linder and Schmidt [19]; ▽, Nishimura et al. [21]; ○, Brunger et al. [20]. Theory: dotted line, Berman et al. [22]; dashed line, Morrison and Trail [23]; unbroken line, present results. The asterisk gives the position of the excitation threshold.

2.3. *Vibrational excitation of the physisorbed molecule*

We follow the same lines (CAM approach) as our earlier studies of electron–N_2 vibrational excitation [14–16]. The effects of the electron–surface interaction potential $V_{e\text{–}S}(z)$, where z is the electron–surface distance, are added to the Hamiltonian used above. This potential is taken from Ref. [29] for the silver surface. It modifies the coupled equations for the radial wave functions $\phi^{v}_{l,m}(r)$, which are now also coupled inside each v block by the $V_{e\text{–}S}(z)$ interaction potential. Because of this coupling, the various electron angular modes [spherical harmonics in the expansion (1)] are coupled for all r values and hence the

S-matrix cannot be extracted in this angular basis which remains coupled at infinity. One thus defines a new angular basis set which diagonalises the entire potential at infinity and in which the S-matrix can be extracted. These angular modes, called 'adiabatic angular modes', take into account the asymmetry introduced by the surface. The adiabatic angular modes form two groups that asymptotically correspond to scattering into the metal or into the vacuum. From the scattering S-matrix, one can define the vibrational inelasticity for the collision energy E and for the $(v\rightarrow v')$ vibrational excitation:

$$I_{v\rightarrow v'}(E)=\sum_{n_\mathrm{i},n_\mathrm{f}}|S^{v\rightarrow v'}_{n_\mathrm{i},n_\mathrm{f}}(E)|^2, \qquad (4)$$

where n_i and n_f are the indices of the electron adiabatic angular modes for the initial and final states. $S^{v\rightarrow v'}_{n,n'}$ is the S-matrix element for the $(v\rightarrow v')$ vibrational excitation and for the n, n' angular modes. The inelasticity represents an average excitation probability for the collision. We did not try to compute differential excitation cross-sections from the S-matrix but rather determined 'summed cross-sections', $\sigma_\mathrm{AB}(v\rightarrow v')$ with A, B = M or V (see the discussion in Refs. [14,15]). Summed cross-sections are obtained from the differential cross-sections by integrating over the final angle and averaging over the initial angle; the integration and the average are performed either over the vacuum part (V) or over the metal part (M) of space. One thus obtain the VV summed cross-section which corresponds to a usual scattering experiment in which both the incident and outgoing electrons are in the vacuum part of space. The VM summed cross-section corresponds to an electron incident from the vacuum and an outgoing electron in the metal; this process is present in a usual scattering experiment but is not observed. The MV and MM summed cross-sections correspond to incident electrons coming from the metal, i.e., to experiments performed with hot metal electrons. These summed cross-sections are determined using the simple method of Refs. [14,15], with surface transmission probabilities:

$$\sigma_\mathrm{AB}(v\rightarrow v')=\frac{\pi}{k_\mathrm{i}^2}\,g_\mathrm{A}g_\mathrm{B}I_{v\rightarrow v'} \quad \text{with A, B} = \text{V or M}, \qquad (5)$$

where k_i is the electron momentum in the incident channel and g_V and g_M are the classical sharing factors between the vacuum (V) and the metal (M) sides [14,15]. The classical sharing factor g_V (g_M) [14,15] is equal to the probability of an electron emitted from the molecular centre with an angular distribution given by the dominant angular momentum of the resonance (pσ in the molecular frame in the present case) to be in the vacuum (or metal) at infinity. For a given electron energy, the sum of g_V and g_M is equal to one. These factors depend on: (1) the relative importance of the electron energy and of the surface potential at the centre of the molecule; and (2) the orientation of the molecular axis with respect to the surface normal. In Eq. (5), the two factors g_A and g_B are evaluated at the incident and outgoing energies, respectively.

These calculations were performed for two different orientations of the molecular axis with respect to the surface: perpendicular and parallel. In the perpendicular geometry, most of the molecular symmetry is preserved and, in the close-coupling expansion, m is still a good quantum number. In the parallel geometry, there is symmetry only with respect to the plane perpendicular to the surface that contains the molecular axis (see the discussion in Ref. [37]).

3. Vibrational excitation of an H_2 molecule adsorbed on a free-electron metal

3.1. Vibrational inelasticities

Fig. 3 presents the inelasticities $(v=0)\rightarrow(v'=1, 2, 3)$ for an H_2 molecule physisorbed on the metal with its axis normal to the surface. Different molecule–surface distances, $Z=4a_0$, $15a_0$ and infinity (measured from the surface image reference plane), are presented to illustrate the effect of varying the strength of the perturbation introduced by the surface. Indeed, in a real system, the molecule–surface distance is fixed (typically in the range of $4a_0$ for a copper jellium surface [38]) and the variation shown in Fig. 3 is only for illustrative purposes. First one can notice that, for a finite molecule–surface distance, the vibrational inelas-

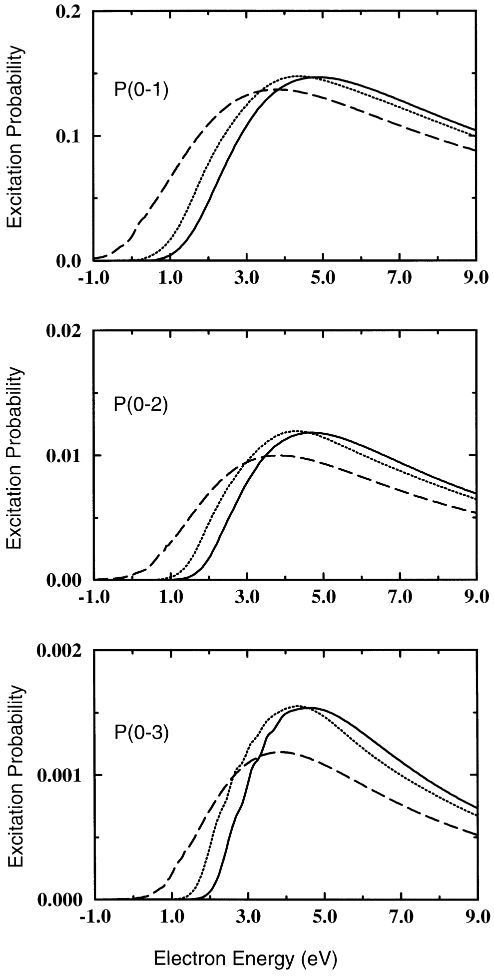

Fig. 3. Vibrational excitation probabilities for an H_2 molecule in front of a silver metal surface as a function of the electron collision energy. The three panels correspond to the excitation from the $v=0$ vibrational level to the $v'=1$, 2 and 3 levels. The molecular axis is normal to the surface and the molecule is located at a distance $Z=4a_0$ (dashed line) and $Z=15a_0$ (dotted line) from the surface image plane. The unbroken line is the result for a free molecule (infinite Z).

ticity does not go to zero for negative energies. This is a direct consequence of the presence of the surface. Negative energies correspond to electrons in the metal that cannot escape into vacuum because of energy; however, for a finite Z distance, they can tunnel to the molecule, induce vibrational excitation and go back into the metal with a lower energy.

Fig. 3 shows that the inelasticity does not appear to be much influenced by the presence of the surface, its magnitude is only slightly changed by the adsorption. The main effect of the surface is to shift the inelasticity towards lower energies. This feature, already found for the N_2^- ($^2\Pi_g$ and $^2\Sigma_u$) resonances, is due to the image charge interaction between the negative molecular ion and the metal surface. The magnitude of the shift can be estimated by the value of the potential at the centre of the molecular ion (roughly equal to $-1/4Z$). The weak effect of the surface on the inelasticity can be linked with the properties of the H_2^- ($^2\Sigma_u$) resonance. It is very broad in the free molecule and so it would require a very strong perturbation by the surface to modify its width significantly. On the other hand, the surface interaction potential induces an energy shift in the resonance, which is readily seen.

The results for the inelasticity in the case of a molecular axis parallel to the surface (not shown here) were found to be very similar to those in Fig. 3. This can also be linked with the properties of the H_2^- ($^2\Sigma_u$) resonance. The above discussion of the resonance energy shift is independent of the molecular orientation. The coupling between the metal electronic states and the resonance depends on the molecular orientation (see, for example, Ref. [37]). However, since this coupling is found to have only a very limited effect on the resonance width, it does not lead to any significant change in the inelasticity with the molecular orientation.

3.2. Vibrational excitation summed cross-sections

The vibrational excitation summed cross-section (perpendicular geometry) for the $(v=0)\rightarrow(v'=1)$ excitation is presented in Fig. 4 for three different molecule–surface distances: $Z=4a_0$, $15a_0$ and infinity (for infinite Z, the summed cross-section is equal to one-quarter of the total vibrational excitation cross-section for the free molecule). The shape of the VV summed cross-section in Fig. 4 appears to vary only slightly with the molecule–surface distance: the classical sharing factors in Eq. (5) strongly reduce the cross-section at low energies. They thus remove most of the downward shift visible in Fig. 3. This mainly results in a

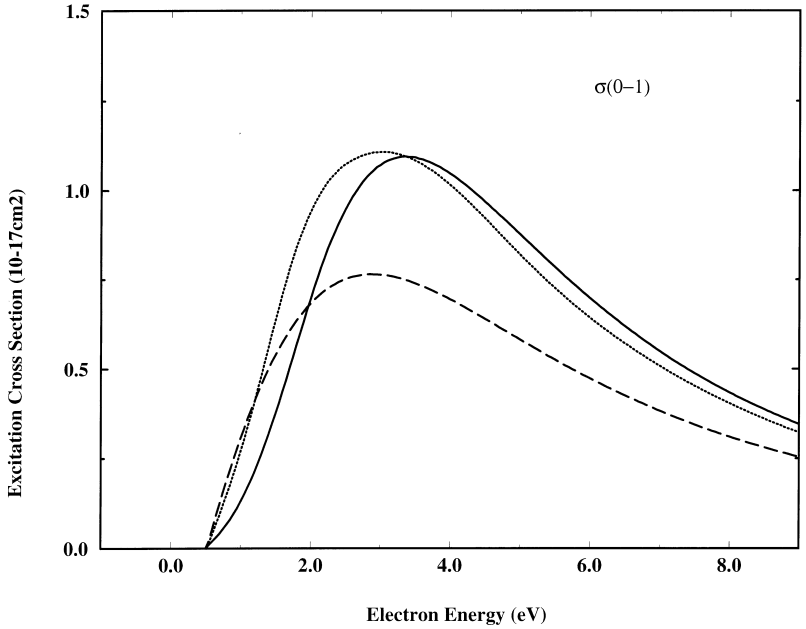

Fig. 4. Vibrational excitation ($v=0 \to v'=1$) summed cross-section (VV process, in 10^{-17} cm^2) for an H_2 molecule in front of a silver metal surface as a function of the electron collision energy. The internuclear axis is normal to the surface. The molecule is located at a distance $Z=4a_0$ (dashed line) and $Z=15a_0$ (dotted line) from the surface image plane. The unbroken line is the result for a free molecule (infinite Z).

decrease in the summed cross-section as the molecule–surface distance decreases. Fig. 5 presents the four summed cross-sections VV, VM, MV and MM for a molecule–surface distance of $4a_0$ and the molecular axis normal to the surface. The relative magnitude of these summed cross-sections depends on two factors: (1) the incident energy factor in Eq. (5), which strongly favours the VV and VM processes; and (2) the classical sharing factors which, at low energy, favour the M side. The latter terms are also responsible for the different energy dependencies and, in particular, for the different thresholds of the various summed cross-sections.

All the results presented above are for molecules with their molecular axis normal to the surface. As discussed above, the inelasticities do not depend much on the molecular axis orientation; however, the summed cross-sections depend strongly on orientation via the classical sharing factors in Eq. (5). The pσ wave associated with the $^2\Sigma_u$ resonance is peaked along the molecular axis. As a consequence, for a molecular axis parallel to the surface, the attractive surface potential results in a strong dominance of the g_M factor over the g_V factor, particularly at low collision energies. This explains the very large and energy-dependent difference in magnitude between the VV summed cross-sections for the parallel and perpendicular geometries presented in Fig. 6.

The interaction of H_2 molecules with surfaces has been studied in detail in the case of a few metals. Study of the rotational excitation spectra and of the low-energy molecule–surface scattering showed the characteristics of the rotation of H_2 molecules on a surface; i.e., of the anisotropy of the molecule–surface interaction. Experimental studies of the electron impact rotational excitation of physisorbed H_2 molecules showed that the molecular rotation is not hindered and that the rotation characteristics are very close to those of the free molecule (see Refs. [26,39–41] for various surfaces: silver surface [39], Cu(100) surface [40], graphite surface [41]). Detailed analysis has shown that there exists a small anisotropy of the H_2–metal interaction [38,42]; in the case of

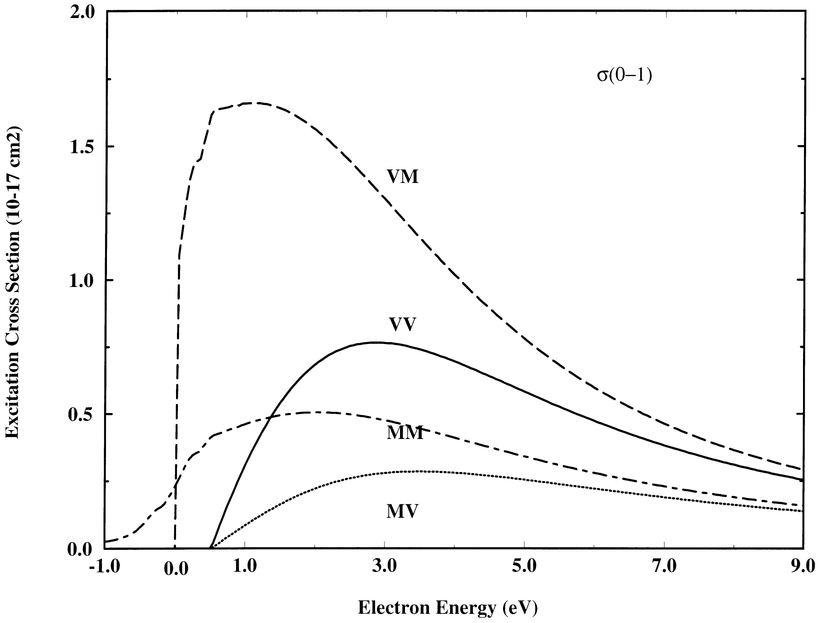

Fig. 5. Vibrational excitation ($v=0\rightarrow v'=1$) summed cross-sections (VV, VM, MV and MM processes, in 10^{-17} cm^2) for an H_2 molecule in front of a silver metal surface as a function of the electron collision energy. The internuclear axis is normal to the surface and the molecule is located at a distance $Z=4a_0$ from the surface image plane.

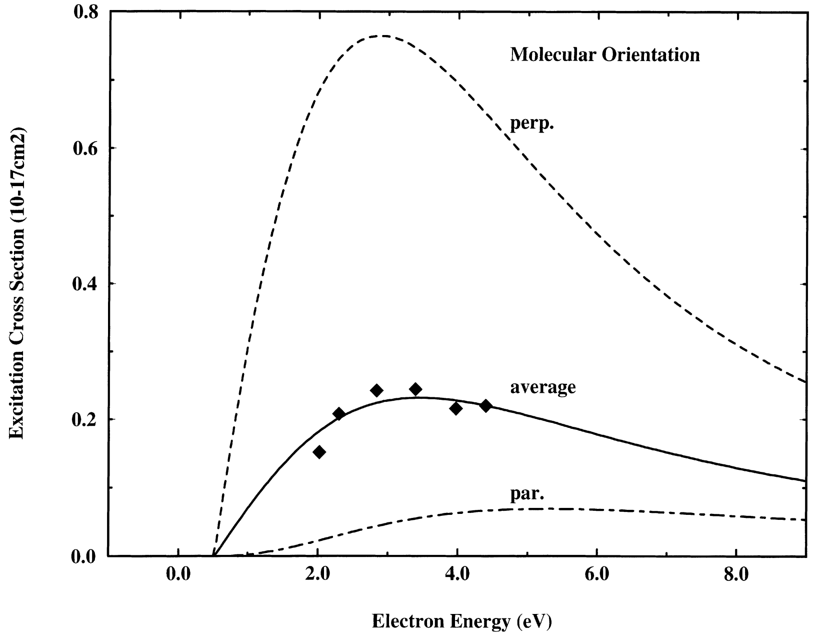

Fig. 6. Vibrational excitation ($v=0\rightarrow v'=1$) summed cross-sections (VV process, in 10^{-17} cm^2) for an H_2 molecule in front of a silver metal surface as a function of the electron collision energy. The molecular axis is normal to the surface (dashed line) or parallel to the surface (dashed–dotted line). The unbroken line represents the angular averaged summed cross-section compared with the normalised results of Demuth et al. [5] (◆).

Cu(100), in particular, it leads to a slight preferential orientation of the molecular axis normal to the surface [38].

The present study of vibrational excitation is performed within the sudden approximation for the rotational motion; i.e., the molecular axis orientation is assumed to be fixed during the collision. This is justified in view of the short resonance lifetime. The vibrational excitation cross-section should therefore be averaged over the distribution of molecule orientations of the target. Assuming this distribution to be isotropic in agreement with the experimental observation of quasi free rotational motion of the physisorbed molecules, one obtains the averaged vibrational excitation summed cross-section that is presented in Fig. 6. Its shape is mainly determined by the perpendicular geometry. However, its magnitude is much smaller than that of the perpendicular geometry. Fig. 7 presents further results for this averaged cross-section for the $(v=0)\rightarrow(v'=1, 2, 3)$ excitations for three different molecule–surface distances ($4a_0$, $15a_0$ and infinity). One can see that the energy dependence of these averaged cross-sections is only weakly modified by the presence of the surface. In contrast, the absolute magnitude of the excitation cross-sections decreases strongly in the presence of the metal surface. One can also notice that the small oscillations visible in the $(v=0)\rightarrow(v'=3)$ excitation for the free molecule and attributed to the longer resonance lifetime at large R [35,36] are almost suppressed in the case of the physisorbed molecule, most probably due to the shortening of the resonance lifetime at large R. Indeed, the interaction with the surface, although unable to alter the resonance lifetime around the equilibrium distance of the molecule, is able to shorten it in the R region where this lifetime is long.

The averaged cross-section, taking into account the molecular orientation, can be compared with experimental results. Fig. 6 compares it with the scaled results of Demuth et al. [5]. This comparison is not fully justified since it compares a summed cross-section to the differential cross-section at a given angle; it implicitly assumes that the angular dependence of the differential cross-section, dominated by the resonant process, does not depend much on the collision energy. The energy dependencies of the two cross-sections are seen to be quite similar. In particular, the fact that the excitation cross-section for the physisorbed molecule is very close to that for the free molecule is fully confirmed by the present results.

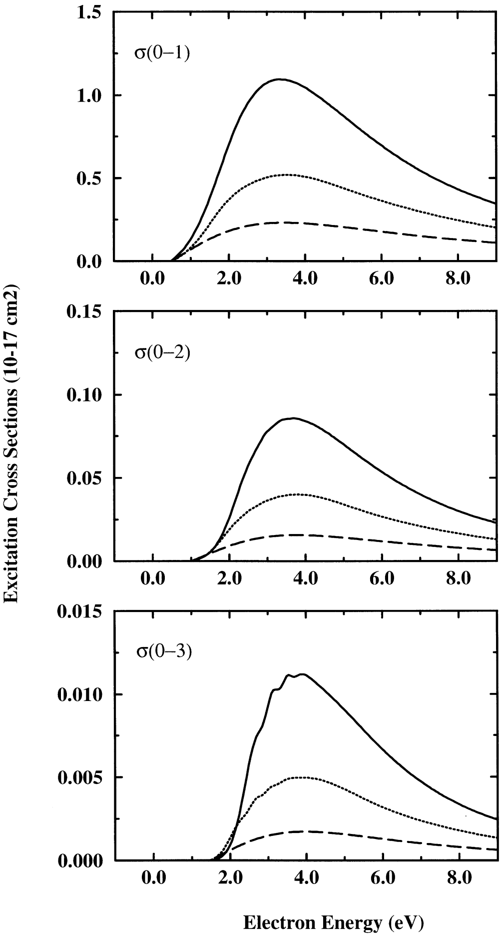

Fig. 7. Vibrational excitation summed cross-sections (VV process, in 10^{-17} cm^2) for an H_2 molecule in front of a silver metal surface as a function of the electron collision energy. The three panels correspond to the excitation from the $v=0$ vibrational level to the $v'=1$, 2 and 3 levels. The summed cross-section has been averaged over the orientation of the molecular axis (free rotation approximation). The molecule is located at a distance $Z=4a_0$ (dashed line) and $Z=15a_0$ (dotted line) from the surface image plane. The unbroken line is the result for a free molecule (infinite Z).

Finally, we discuss the overtone excitation ratio $R_{v'}$. We define this as the ratio between the VV summed cross-section for vibrational excitation to a level v' to that for vibrational excitation to the level $v'=1$:

$$R_{v'}=\frac{\sigma_{\mathrm{VV}}(0\rightarrow v')}{\sigma_{\mathrm{VV}}(0\rightarrow 1)}. \qquad (6)$$

The cross-sections are taken at their maximum. For the physisorbed molecules, the ratios are evaluated from the summed cross-sections averaged over the molecular orientation. The overtone ratios are presented in Table 1 for various sets of results: experiment and theory for the free molecule, and present results for the free and physisorbed molecule. The present results for the free molecule are seen to reproduce nicely the experimental results of Allan [35], which span a large range of final vibrational levels, once again confering confidence to the present description of the electron–free H_2 interaction. For the physisorbed molecules, the overtone ratio is found to be smaller than that for the free molecule. Usually, this feature has been considered as a sign of an increase in the resonance width due to the presence of the metal surface [6]. However, it has been shown that the anisotropy of space introduced by the surface also deeply influences the overtone excitation ratio [7]. Indeed, when the resonance is located at low energy, such as in the present case, the sharing of the inelasticity between the vacuum and the metal channels results in a decrease of the vibrational excitation as observed in a scattering experiment (VV process); i.e., in a decrease of the overtone excitation ratio as defined by Eq. (6). In the present system, the inelasticities for the physisorbed molecules are slightly smaller than for the free molecule (see Fig. 3) and this is the direct consequence of a decrease of the resonance lifetime at large R (see also the disappearance of the oscillations in the $v'=3$ channel). As for the overtone excitation ratios, their decrease is due to both an effect of the V–M sharing and an increase of the resonance width at large R.

4. Concluding remarks

We present a theoretical study of the resonant vibrational excitation by low-energy electron impact of H_2 molecules physisorbed on free-electron metals. The study uses ab initio R-matrix results on electron–free molecule scattering to parameterise the electron–free H_2 molecule interaction. This parameterisation is then used to describe electron–H_2 scattering in the presence of a free-electron metal surface, taken with the characteristics of silver metal. The low-energy vibrational excitation process is dominated by the short-lived $^2\Sigma_u$ resonance of H_2. When the H_2 molecule is physisorbed on a metal surface, the molecular environment modifies the scattering properties of the molecule. The main points are:

- the resonance energy is lowered;
- there is a very limited change in the resonance lifetime, due to its very small value in the free molecule;
- the shape of the excitation cross-section as it would be observed in a scattering experiment is very close to that for a free molecule;
- the strength of the excitation cross-section and, in particular, the overtone excitation ratio are decreased; and
- the present results are found to reproduce the main features of the experimental results of Demuth et al. [5].

After studying different molecules with different

Table 1
Overtone excitation ratios $R_{v'}$ [see text and Eq. (6) for definition] obtained in various experimental and theoretical studies for free and physisorbed molecules

	$v'=2$	$v'=3$	$v'=4$	$v'=5$	$v'=7$
Experiment: Ehrhardt et al. [18]	0.077	0.008			
Experiment: Allan [35]	0.075	0.0075	0.0017	0.00067	0.00028
Theory: Berman et al. [22]	0.076	0.018	0.0051		
Present theory: free molecule	0.078	0.010	0.0020	0.00054	0.00020
Present theory: physisorbed molecule, $Z=4a_0$	0.068	0.0074	0.0012	0.00023	0.000055

resonance characteristics physisorbed on a free-electron metal surface ($^2\Pi_g$ and $^2\Sigma_u$ resonances of N_2 [7,16]; $^2\Sigma_u$ resonance of H_2), one can draw some general conclusions on the effects of physisorption on the resonant vibrational excitation process. These are: (1) the resonance energy is lowered; (2) the resonance width is increased — although, this is only significant if the resonance width is not too large in the free molecule; and (3) for low-energy processes, the excitation cross-sections and the overtone excitation ratios decrease due to the sharing of the vibrational excitation process between the metal and the vacuum channels.

References

[1] G. Schulz, Rev. Mod. Phys. 45 (1973) 423.
[2] R. Palmer, P.J. Rous, Rev. Mod. Phys. 64 (1992) 383.
[3] L. Sanche, J. Phys. B 23 (1990) 1597.
[4] L. Sanche, M. Michaud, Phys. Rev. Lett. 47 (1981) 1008.
[5] J.E. Demuth, D. Schmeisser, Ph. Avouris, Phys. Rev. Lett. 47 (1981) 1166.
[6] A. Gerber, A. Herzenberg, Phys. Rev. B 31 (1991) 393.
[7] D. Teillet-Billy, V. Djamo, J.P. Gauyacq, Surf. Sci. 269/270 (1992) 425.
[8] P.J. Rous, Surf. Sci. 260 (1992) 361.
[9] J.W. Gadzuk, J. Chem. Phys. 79 (1983) 3982.
[10] P.J. Rous, Surf. Sci. 279 (1992) L191.
[11] A.G. Borisov, A.K. Kazansky, J.P. Gauyacq, Phys. Rev. Lett. 80 (1998) 1996.
[12] D. Teillet-Billy, J.P. Gauyacq, Surf. Sci. 239 (1990) 343.
[13] J.P. Gauyacq, Dynamics of Negative Ions, World Scientific, Singapore, 1987.
[14] V. Djamo, D. Teillet-Billy, J.P. Gauyacq, Phys. Rev. Lett. 71 (1993) 3267.
[15] V. Djamo, D. Teillet-Billy, J.P. Gauyacq, Phys. Rev. B 51 (1995) 5418.
[16] F. Bertolucci, R. Franchy, J.A.M.C. Silva, A. Moutinho, D. Teillet-Billy, J.P. Gauyacq, J. Chem. Phys. 108 (1998) 2251.
[17] D.J. Birtwistle, A. Herzenberg, J. Phys. B 4 (1971) 53.
[18] H. Ehrhardt, L. Langhans, F. Linder, H.S. Taylor, Phys. Rev. 173 (1968) 222.
[19] F. Linder, H. Schmidt, Z. Naturforsch. 26a (1971) 1603.
[20] M.J. Brunger, S.J. Buckman, D.S. Newman, D.T. Alle, J. Phys. B 24 (1991) 1435.
[21] H. Nishimura, A. Danjo, H. Sugahara, J. Phys. Soc. Jpn. 54 (1985) 1757.
[22] M. Berman, C. Mündel, W. Domcke, Phys. Rev. A 31 (1985) 641.
[23] M.A. Morrison, W.K. Trail, Phys. Rev. A 48 (1993) 2874.
[24] D.T. Stibbe, J. Tennyson, J. Phys. B 31 (1998) 815.
[25] R.K. Nesbet, Comments At. Mol. Phys. 11 (1981) 25.
[26] M. Gruyters, K. Jacobi, Chem. Phys. Lett. 225 (1994) 309.
[27] J.P. Gauyacq, B. Bahrim, A. Djabri, V. Djamo, D. Teillet-Billy, in: P.G. Burke, C. Joachain (Eds.), Photon and Electron Collisions with Atoms and Molecules, Plenum Press, New York, 1997, p. 69.
[28] R.K. Nesbet, Phys. Rev. A 19 (1979) 551.
[29] P.J. Jennings, R.O. Jones, M. Weinert, Phys. Rev. B 37 (1988) 6113.
[30] L.A. Morgan, J. Tennyson, C.J. Gillan, Comput. Phys. Commun. 114 (1998) 120.
[31] D.T. Stibbe, J. Tennyson, Phys. Rev. Lett. 79 (1997) 4116.
[32] W. Kolos, L. Wolniewicz, J. Chem. Phys. 46 (1967) 1426.
[33] D. Teillet-Billy, L. Malegat, J.P. Gauyacq, J. Phys. B 20 (1987) 3201.
[34] N. Lorente, D. Teillet-Billy, J.P. Gauyacq, J. Chem. Phys. 111 (1999) 7075.
[35] M. Allan, J. Phys. B 18 (1985) L451.
[36] M. Berman, C. Mündel, W. Domcke, Phys. Rev. A 31 (1985) 641.
[37] V. Djamo, D. Teillet-Billy, J.P. Gauyacq, Surf. Sci. 346 (1996) 253.
[38] L. Wilzén, F. Althoff, S. Andersson, M. Persson, Phys. Rev. B 43 (1991) 7003.
[39] Ph. Avouris, D. Schmeisser, J.E. Demuth, Phys. Rev. Lett. 48 (1982) 199.
[40] S. Andersson, J. Harris, Phys. Rev. Lett. 48 (1982) 545.
[41] R.E. Palmer, R.F. Willis, Surf. Sci. 179 (1987) L1.
[42] A.J. Berlinsky, Phys. Rev. B Rapid Commun. 26 (1982) 443.