

Molecular rotation induced by inelastic electron tunneling

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(Received 7 June 2000; revised manuscript received 25 September 2000)

Electron tunneling from a scanning tunneling microscope tip has recently been shown to induce reversible rotation of O₂ molecules chemisorbed on Pt(111) [B. C. Stipe *et al.*, *Science* **279**, 1907 (1998)]. This process is interpreted as proceeding via the transient capture of the tunneling electron by the adsorbate. A finite angular momentum can be transferred in a resonant electron-molecule scattering, leading to an efficient rotational excitation. This process is a direct consequence of the electronic structure of the resonance and of angular momentum conservation; it does not require a long resonance lifetime to be efficient.

The manipulation of molecules by a scanning tunneling microscope (STM) tip has recently become a very active research field;¹ various possible actions have been reported: atom displacement,² molecule fragmentation,³ single molecule dissociation,⁴ desorption,⁵ and more recently adsorbate rotation.⁶ In many cases, the rearrangement or movement of molecules (atoms) on the surface is directly induced by the electrons tunneling between the STM tip and the surface. In a recent experimental study on the O₂/Pt(111) system,⁶ it was shown that tunneling electrons can induce the rotation of the O₂ molecule. At its equilibrium position in the Pt(111) three-fold hollow sites, the O₂ molecule is oriented along one of three equivalent azimuthal directions, with its axis slightly tilted away from the surface. Because of the tilt angle, the molecule image appears pear-shaped, allowing one to recognize the orientation of the axis. The adsorption geometry has been confirmed by a recent density-functional theory study.⁷ Stipe *et al.*⁶ showed that the tunneling current is inducing the rotation of the molecular axis, i.e., the jump of the molecule between equilibrium orientations. They analyzed the rate for molecular rotation as a function of the STM bias and current. They showed that the molecule rotation is caused by the inelastic tunneling of low-energy electrons and they could characterize the rotation induced by a single electron or by a few successive electrons. These results demonstrate that it is possible to provoke a reversible change in the surface structure on the atomic scale with a high transition rate and a small STM potential bias.

In the present work, we show how these experimental data can be interpreted as the result of *resonant* inelastic scattering of the electrons by the molecule: the electrons tunneling from the tip are captured by the molecule to form a transient negative ion, a molecular resonance, and are then scattered into the substrate. We show how the specificities of low-energy resonant electron scattering, in particular the need to take into account angular momentum conservation, can lead to a very efficient rotational excitation of the adsorbed molecules, even in the case of a short-lived resonance.

The energy transfer during an electron-molecule collision is very efficiently induced by resonances, i.e., by the possibility for the collisional electron to be temporarily trapped by

the target molecule. This feature is very well known for free molecules⁸ as well as for molecules adsorbed on solid surfaces, where it was shown to lead to a variety of inelastic processes.^{9–11} Resonant scattering can also induce an efficient rotational excitation in electron collisions with free or adsorbed molecules. In resonant scattering, the incident electron is captured into a molecular orbital of a well-defined symmetry associated with a well-defined angular momentum l or with contributions from a very limited number of angular momentum. There is thus a finite angular momentum of the order of a few atomic units that is brought and carried away by the resonantly scattered electron, leading via the addition (subtraction) of angular momentum to a net momentum transfer to the target molecule. The rotational excitation resulting from this angular momentum exchange can be treated in the rotational sudden approximation,¹² valid for collision times shorter than the rotation time. The scattering amplitude is proportional to the matrix element M_{ij} .¹²

$$M_{ij} = \langle \Psi_j(\theta, \phi) | A^*(\mathbf{k}_f) A(\mathbf{k}_i) | \Psi_i(\theta, \phi) \rangle, \quad (1)$$

where $\Psi_{i,j}$ are the initial and final rotational states of the molecule (molecular axis coordinates: θ, ϕ). $A(\mathbf{k}_{i,f})$ is the angular shape of the resonant orbital as a function of the direction of the electron in the initial (i) or final (f) state. In resonance scattering, the angular shape A can be represented by a single spherical harmonic (in the molecular frame) or by the superposition of a very small number of spherical harmonics.

It is noteworthy that the excitation defined in Eq. (1) is independent of the resonance lifetime. This excitation process is thus quite different from other resonant processes where there is a transient force acting during the resonance lifetime and which then depend in a crucial way on the resonance lifetime. This is, for example, the case in vibrational excitation, where the molecule stretches (or contracts) during the resonance lifetime due to the difference between the potential energy curves of the ground and resonant state. This situation has been studied in detail in the case of STM induced vibrational motion¹³ and bond breaking;¹⁴ one can also mention similar studies of the desorption induced by electronic transitions¹⁵ or of the electron impact vibrational

excitation^{16–18} processes. For a freely rotating molecule, there is no force acting on the rotation during the resonance lifetime and so the only possible excitation process is the one described by Eq. (1). The situation of an adsorbed molecule could be different if the geometry of adsorption is different in the ground and resonance states. Then, a torque is acting on the molecular axis during the collision. Attempts to model the experimental results from Ref. 6 with an approach similar to vibrational excitation, i.e., including a transient torque, could only represent the experimental observations when introducing an extremely large unphysical transient torque. In the process studied here, the excitation is a direct consequence of the fact that the electron is bringing to the molecule a well-defined quantified angular momentum, equal to a few \hbar and that this angular momentum transfer is significant for the molecule rotation.

The O₂ adsorption has been the subject of many studies. Two chemisorbed species have been characterized.^{4,7,19–23} In the experiment of Stipe *et al.*⁶ the molecules are adsorbed in the fcc threefold hollow sites of the Pt(111) surface. The molecule is lying almost flat on the surface, its axis making a small angle Θ_T with the surface plane. This tilt angle has been theoretically determined around 10° (Refs. 7 and 22) and observed experimentally to be a small angle.²³ The molecular axis has thus three equivalent orientations on the surface, 120° away one from the other. However, the O₂ molecule being homonuclear, one can also consider that the molecule goes from one equilibrium *azimuthal* orientation to the next by a rotation of only 60°. In this case, the rotation from one azimuthal orientation to the next has to be associated with a change of the tilt angle, from Θ_T to $-\Theta_T$; the rotation is also associated with a small translation of the molecule on the surface. Such a picture with six equivalent molecular orientations is particularly well founded in the present case of a very small tilt angle. In the following, we consider that the O₂ molecule has six equilibrium azimuthal orientations.

The rotational excitation of the O₂ molecule on Pt(111) is modeled as follows: (i) the molecule is adsorbed on the surface with a small tilt angle Θ_T , (ii) the molecule rotational motion is governed by a potential that is periodic in ϕ , the azimuthal angle with six equilibrium positions: $U(\phi) = U_0(1 + \cos 6\phi)$, (iii) the effect of the initial electronic angular momentum of the molecule is neglected, (iv) the electrons from the tip come along the normal to the surface, are captured to form a transient negative ion, and are then re-emitted in all directions, according to the resonance orbital angular shape. The π^* orbital of O₂ is located around the Fermi level in the O₂/Pt(111) system²⁴ and it is assumed to be the active resonant orbital for small STM voltage biases. Its angular shape A is approximated by a $d\pi$ wave as in the free O₂⁻ molecule, i.e., it is equal to a spherical harmonic Y_{lm} , with $l=2$, $m=\pm 1$, in the molecular frame.

In a first step, we determine the eigenvalues and eigenfunctions for the hindered rotational motion in the potential $U(\phi)$ with a tilt angle Θ_T . These are obtained by the numerical solution of the Schrödinger equation for the molecule rotation in the potential $U(\phi)$. The potential $U(\phi)$ presents six potential wells separated by a barrier equal to $2U_0$. The eigenfunctions are mixtures of states localized inside all the potential wells, because of the possibility of

quantum tunneling from one potential well to the next. By linear combination of these states, we form states labeled by (n, j) localized inside the potential well (j) and corresponding to the same n th state. Their energy E_{nj} is only a function of n and the various j states are *a priori* coupled by tunneling. We then evaluate the excitation (or de-excitation) probabilities $P_{n'j'nj}$ by resonant electron scattering from one state (n, j) to another (n', j') using expression (1) and a $d\pi$ wave angular shape for $A(\mathbf{k})$ (in fact, we sum the contributions from the two degenerate π orbitals):

$$P_{n'j'nj} = \frac{\int d^2\mathbf{k}_f |\langle \Psi_{n'j'}(\theta, \phi) | A^*(\mathbf{k}_f) A(\mathbf{k}_i) | \Psi_{nj}(\theta, \phi) \rangle|^2}{\int d^2\mathbf{k}_f \sum_{n', j'} |\langle \Psi_{n'j'}(\theta, \phi) | A^*(\mathbf{k}_f) A(\mathbf{k}_i) | \Psi_{nj}(\theta, \phi) \rangle|^2}, \quad (2)$$

where the integral over \mathbf{k}_f runs over all possible directions of \mathbf{k}_f . \mathbf{k}_i is along the surface normal. Due to the strong localization of the low-lying states (n, j) inside each well, the excitation probability is only significant for $j=j'$, i.e., the rotational excitation only occurs inside each well. For the excitation rates $I_{n'j'nj}$, we assume that the energy distribution of the tunneling electrons is constant between zero and V :

$$I_{n'j'nj} = P_{n'j'nj} \left(\frac{V - E_{n'j'} + E_{nj}}{V} \right) \left(\frac{I}{e} \right) \quad \text{for } V > E_{n'j'} - E_{nj}, \quad (3)$$

and zero otherwise. I is the tunneling current and e is the electron charge. Equation (3) implicitly assumes that the tunneling current I is entirely due to resonant scattering through the ($2\pi^*$) orbital.

The molecular jump from one equilibrium position to the next then appears as due to the rotational excitation inside a well by electron impact, followed by a quasifree rotation when the excitation energy is large enough. The quasifree rotation rate from one well to the next is taken equal to $\omega/2\pi$ where ω is the energy quantum inside the wells. This rotation being very fast, the final results do not depend on the precise value of the quasifree rotation rate. In the following, we neglect the tunneling of the molecule between the potential wells; we assume that the levels with an energy above the potential barrier as well as the last one below the barrier rotate quasifreely and all the others remain inside the same potential well.

Using all the above rates, we can write rate equations describing the evolution of the populations C_{nj} of the various states and containing the excitation and deexcitation terms by electron impact [expression (3)], the free rotation terms for the states high enough in energy and a relaxation rate $R_{n'n}$ from states (n, j) to the states (n', j) that are lower in energy inside each well. The relaxation rate $R_{n'n}$ is taken independent of n and n' . From the rate equation, we get the populations as a function of time. We also get the rate for a jump from one equilibrium orientation to the next (effective rotation rate K_R) as the smallest nonzero eigenvalue of the matrix describing the population evolution.

We used the relaxation rate R and the barrier separating the potential wells as adjustable parameters. The results shown below are obtained for a potential barrier $2U_0$ of 0.22

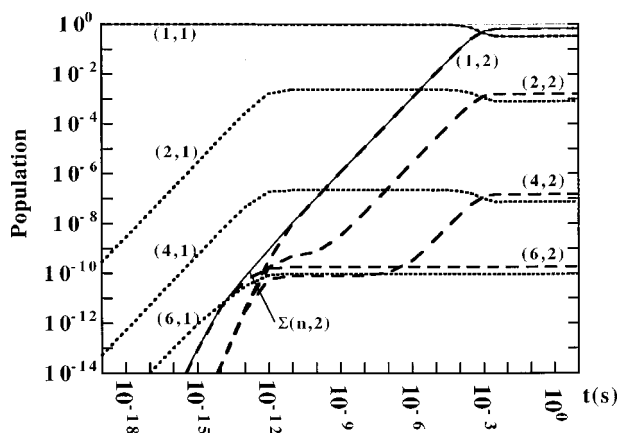


FIG. 1. Population of the various rotational levels as a function of time (for clarity sake, only a few levels are presented). The system is initially in the lowest level ($n=1$) in well $j=1$. Dotted lines are the $(n,1)$ levels. The dashed lines are the $(n,2)$ levels. The full line is the sum of the populations in the $(n,2)$ levels, i.e., number of molecules in an azimuthal orientation different from the initial one.

eV and a relaxation rate, $R_{n'n}$, of $1.2 \times 10^{11} \text{ s}^{-1}$. The latter is in the typical range expected for electron-hole pair creation. The results are obtained for a tilt angle equal to 20° . In this case, there are six levels localized in each potential well that are below the potential barrier. The rotational quantum in one well (excitation energy of the first state in each well) is equal to 0.038 eV and the energy threshold to reach the quasifree rotation (energy between the $n=1$ and $n=6$ levels localized inside a well) is equal to 0.167 eV.

The time evolution of the populations is presented in Fig. 1 for a potential bias of 0.25 V and a tunneling current of 10 nA. At time $t=0$, the molecule is in the lowest state localized in the well 1 ($n=1, j=1$). To simplify the discussion, the population in the equivalent wells have been summed up and we present two effective populations: ($j=1$) which corresponds to the initial well and $j=2$ for the others. The time evolution of the populations present different time scales, corresponding to the different orders of magnitude of the various transition rates.

Very early in the time evolution, only the excitation of the molecular rotation by electron impact is efficient and as said above, it mainly excites the levels inside a well, i.e., the $(n, j=1)$ states in the present case. The population of the $(n, j=1)$ levels thus grows linearly in time at the beginning. Around 10^{-11} s the relaxation of the $(n, j=1)$ levels starts to play a role and the $(n, j=1)$ populations reach a transient equilibrium, resulting from the balance between the excitation and de-excitation by electron impact and the intrawell relaxation. In the case illustrated in Fig. 1, this distribution corresponds roughly to a temperature of the order of 75 K, defined on the lowest levels. The levels ($n \geq 6, j=1$) can rotate quasifreely and this leads to the population of the $(n, j=2)$ levels. This appears early as a consequence of the excitation by electron impact. The relaxation acting inside well 2 results in the dominating population of the $(n=1, j=2)$ level among the $(n, j=2)$ levels. In the 10^{-10} – 10^{-4} s range, we can see the population of the (1,2) level growing linearly; this growth corresponds to the O_2 molecule jumping

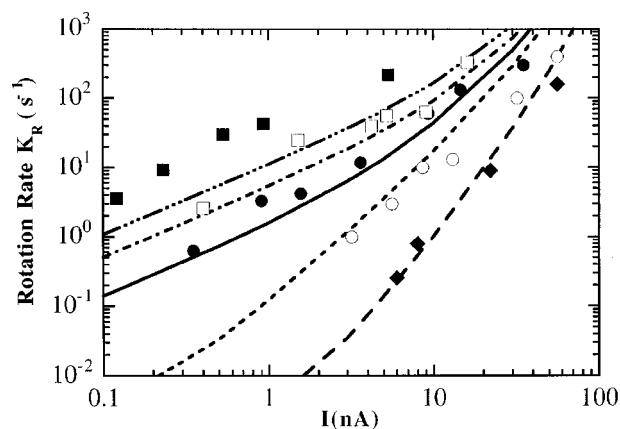


FIG. 2. Effective rotation rate K_R as a function of the tunneling current for various voltage biases, V . Symbols are experiments from Ref. 6; lines are the present results. Diamonds and long dashed line indicate $V=0.1$ V; open circles and short dashed line indicate 0.15 V; filled circles and full line indicate 0.175 V; open squares and dashed-triple dotted line indicate 0.2 V; filled squares and dashed-triple dotted line indicate 0.25 V.

from one equilibrium orientation to another with an effective rotation rate $K_R = 1.65 \times 10^2 \text{ s}^{-1}$ in this case. Finally, around 10^{-2} s, the jumps between the various equilibrium positions are so numerous that a dynamical equilibrium is reached between the wells ($1/3$ for the $j=1$ and $2/3$ for $j=2$), in addition to that inside the wells [relative populations of the (n, j) levels inside a well j].

Figure 2 presents our results for the effective rotation rate K_R as a function of the tunneling current I for various voltage biases V , compared with the experimental data of Stipe, Razaeei, and Ho. One can see that the main features of the experimental results are well reproduced with the set of parameters ($2U_0 = 0.22$ eV, Relaxation rate: $1.2 \times 10^{11} \text{ s}^{-1}$). The linear behavior of $K_R(I)$ for large V at small I corresponds to the molecular rotation induced by a single-electron impact, whereas the larger slopes obtained for smaller biases are associated with the few successive electron impacts needed to induce the O_2 rotation. Rotation induced by a few successive electron impacts is also visible at large I for large V . The change of regime at small intensities occurs in the 0.15–0.2 V range of bias voltage. The order of magnitude of $K_R(I)$ is also well reproduced, except for an underestimation for large potential biases. It is noteworthy that calculations performed with a larger tilt angle Θ_T (equal to 30°), lead to a much better agreement with experiment. This effect can possibly be linked with the fact that, in the experiment, the STM tip is not exactly above the center of the molecule in order to allow for the monitoring of the molecular rotation. This slight asymmetry in the system introduced by the off-center tip position, together with a possible perturbation of the molecule position by the presence of the tip, could be linked to the apparent need for a larger tilt angle in our model.

In conclusion, we have presented theoretical results on the reversible jump of an O_2 molecule between various equivalent molecular orientations on a Pt(111) surface, induced by the inelastic electron tunneling from an STM tip. The resonant process involving the transient $\text{O}_2 \pi^*$ orbital is shown to lead to an efficient rotational excitation, consistent with that observed by Stipe, Razaeei, and Ho.⁶ The picture is that

of a molecule trapped in a rotational potential well and the tunneling electrons excite the molecular rotation inside this well until the energy is large enough to allow a quasifree motion of the molecule; depending on the experimental conditions (STM current and voltage), this occurs via one or a few electron impacts. Our modeling only explicitly considers the azimuthal rotation. In fact, the change of the O₂ molecule orientation *a priori* implies other degrees of freedom. Nevertheless, even in a more sophisticated approach, the process studied here should be present and transfer a significant amount of energy from the electron to the O₂ rotational motion. In this context, one can mention the possible role of the tilt angle which is excited by exactly the same resonant process as the azimuthal movement; the energy transfer from the electron to the tilt motion could eventually result in a molecular azimuthal orientation jump, via the multidimension character of the potential energy surface governing the molecular motion on the surface. In other words, the resonant electron transfers angular momentum to the entire rotational movement of the molecule [multidimensional equivalent of Eq. (1)] and this angular impulse leads to various excitations via the multidimension potential energy surface. The indirect

process involving the tilt motion could increase the efficiency of the resonantly induced rotation of the molecule. In this context, one can mention the experimental study by Stipe, Razaee, and Ho²⁵ of acetylene rotation on Cu(100) induced by tunneling electrons. It shows that the excitation of the acetylene CH stretch is leading to the rotation of the molecule from one equilibrium position to another, confirming the importance of mode coupling in the dynamical evolution following the excitation of a given mode by electron impact.

Finally, one can stress that the present resonant process does not depend on the resonance lifetime. The resonant electron is carrying a finite angular momentum equal to a few \hbar ; it is given to the molecule at the time of the electron capture and taken away by the electron when it leaves, leading to a finite angular momentum transfer. This transfer is a consequence of the resonance character of the process and is always present in any resonant process implying a finite ℓ resonant orbital. There should thus be a possibility of easily inducing reversible modifications on a surface whenever a resonant orbital is present at an energy close to the Fermi energy.

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