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Tunnel heating of a single Xe adsorbate

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In the junction of a scanning tunneling microscope, the energy released by tunneling electron on a single (and the same) Xe adsorbate is calculated taking into account the time dependence of the individual nonresonant electron transfer events inside the tunnel junction. The dissipated energy leads to an apparent and measurable vertical shift of the adsorbate position. The dissipation is governed by a I^{λ} power law with $3.0>\lambda>1.7$ depending on the vibronic coupling coefficient. There is no need to suppose an occupation of the Xe 6*s* excited state to explain such Xe vibration heating phenomenon.

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I. INTRODUCTION

We are interested by the amount of energy released by electrons tunneling in a nonresonant regime through a single (and the same) adsorbate. In the junction of a scanning tunneling microscope (STM), the desorption of a single Xe atom,[1] the rotation at random of O_2 (Ref. 2) and of C_2H_2 (Ref. 3) molecules are now observed experimentally when the energy released by the tunneling electron is enough to change the adsorption site (or conformation) of the adsorbate. Other inelastic processes in an STM junction like the controlled dissociation of C-H (C-D) and the spectroscopy of their stretching modes have been also experimentally observed for C_2H_2 (C_2HD,C_2D_2) (Ref. 4) and theoretically investigated.[5] Several models for the inelastic electron tunneling mechanisms have been suggested for describing the coupling between tunneling electrons and the vibrational modes of an adsorbate.[6–15]

At a low tunnel current intensity I, the adsorbate is slightly "heated" by the tunneling electrons without any desorption or unimolecular reaction.[2] The net result of this heating process is an increase of the fluctuations of the adsorbate position (or conformation) around its equilibrium relative to its thermalization by the surface phonons. In the case of a Xe embedded in an STM junction, a small apparent Δz shift of its average altitude z will result. This small change of altitude z is comparable to the apparent corrugation change observed during STM imaging of adsorbates randomly diffusing on a metal surface.[16] While increasing I, such Δz can be measured by following the time dependence of the STM feedback loop signal.[17]

We provide here a semiclassical description of the inelastic force induced by the tunneling electrons and acting on a single Xe in an STM junction while increasing I. The power dissipated and the resulting average apparent Δz shift for the Xe atom are calculated. In Sec. II, we give detailed derivation of the time averaged tunneling electrons inelastic force acting on the adsorbate. The corresponding time-averaged inelastic electron-adsorbate interaction Hamiltonian is described in Sec. III. For several heights of the STM tip, the shape of the static potential energy curves and the corresponding current intensity curves are compared in Sec. IV. The characteristic features of the Xe displacement Δz, the heating temperature T_{vib}, and the dissipated power P_{diss} associated with the Δz shift are discussed in Sec. V. Finally, some concluding remarks are reported in Sec. VI.

Notice that the tunneling heating phenomenon worked out in this paper must not be confused with a resonant dissociation process where the tip apex of the STM is used as an electron field emission source populating the unoccupied orbitals of the adsorbate.[18,19]

II. TIME-AVERAGED TUNNELING ELECTRON INELASTIC FORCE

In the course of an elementary tunneling event, a tiny amount of energy is lost by the electrons transferred from the tip to the surface via the adsorbate. This energy is mainly released on the adsorbate vibration degrees of freedom. This energy is also released on the electronic cloud giving rise to a small electronic friction effect. We are interested here by the first process where the Xe vibration degree of freedom z in its surface potential well is excited by the tunneling electrons. This excitation does not compared to a direct vibration state to state transition. The reason is that the state to state transition theory is not valid for tunneling electrons from inside the tunnel barrier where the inelastic effects occur. It only applies to ballistic electrons.

For the mechanical effect considered in this paper, there are many ways to demonstrate that the z semiclassical equation of the motion of a Xe atom adsorbed on metal surface is given by[20–22]

$$M\frac{d^2z}{dt^2}=-\nabla U(z)+\eta M\frac{dz}{dt}+F_{in}(t,z). \qquad (1)$$

In Eq. (1), η is the vibration relaxation rate from the Xe towards the surface and $F_{in}(t,z)$ the time-dependent random inelastic force due to the tunneling electrons and acting on the Xe. The ground-state potential energy curve $U(z)$ for the interaction of the Xe with the tip and the surface can be found by semiempirical or *ab initio* approaches (see Fig. 1).[23,24]

Inside the tunnel junction, two random processes are at work to shape $F_{in}(t,z)$. First, to be transferred through the adsorbate, the electrons are delivered one by one to the STM

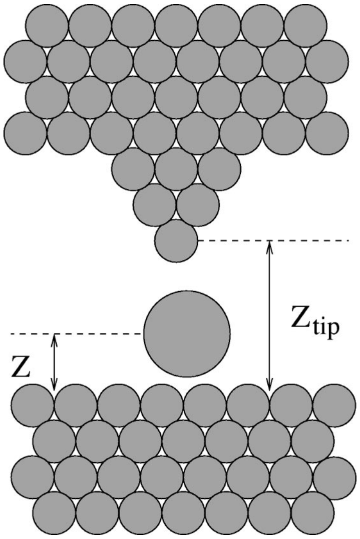

FIG. 1. Schematic representation of a single Xe atom embedded between the Cu(110) surface and tip of an STM junction. The apex of the tip has a ten-Cu-atom pyramidal shape. The surface and the core of the tip are described by four planes; each one contains 50 Cu atoms, and cyclic lateral boundary condition were used (Ref. 23).

junction at random times t_i (Ref. 25) with $f_1(t)$ the normalized envelop of this process. The corresponding Poissonian distribution is usually characterized by the average time interval T separating such delivery events with $T=e/I$. Starting at time t_i, a given elementary elastic electron transfer event has a very short time duration of average τ. Here T is much longer than τ with, for example, for $I=1$ nA through a Xe atom, $T=160$ ps and $\tau=0.4$ fs (see the Appendix). Second, not all the transferred electrons through the adsorbate are inelastically active.[13,26] Therefore, only a very few of the τ intervals have to be taken into account to determine $F_{in}(t,z)$. The time dependence sequence of these events is shown in Fig. 2 with $f_2(t)$ the time distribution of the inelastic events selecting randomly a very few of the elastic event occurrences.

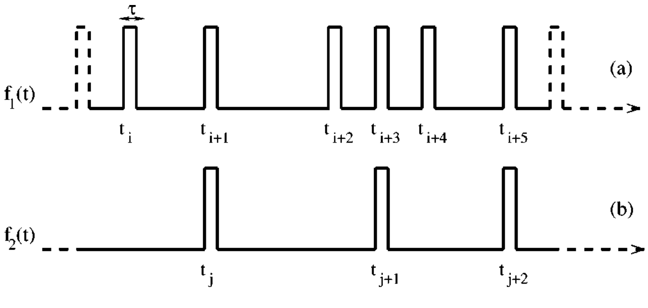

FIG. 2. Schematic representation of the tunnel cyclostationary stochastic process where the average electron transfer duration τ is much smaller than the averaged time interval T separating two successive electron transfer events. (a) The random tunneling elastic electron transfer events for which the occurrences are given by the statistical function $f_1(t)$. (b) The distribution function of active inelastic electron transfer events for which $\hat{H}_{in}(t)$ is switched on, respecting another statistical function $f_2(t)$.

Let us now take $|\psi(z)\rangle$ for the total vibronic state of the tip-adsorbate-surface system and $\hat{H}_{in}(t)$ the Hamiltonian of the inelastic interaction between the Xe z degree of freedom and the tunneling electrons expressed in the interaction representation.[27] $F_{in}(t,z)$ can be written

$$F_{in}(t,z)=\langle\psi(z)|-\nabla_z\hat{H}_{in}(t)f_1(t)f_2(t)|\psi(z)\rangle. \qquad (2)$$

The $f_1(t)f_2(t)$ product gives the "on" and "off" switching sequence of $\hat{H}_{in}(t)$. But in an STM experiment, only the average Δz variation due to $F_{in}(t,z)$ and not its very fast time-dependent variation can be measured. Therefore, only the effect of the time average $\overline{F_{in}(t,z)}$ of this random inelastic events can be observed on Δz. Then, because of the permanent character of the tunnel current I measured outside the tunnel junction, $\overline{F_{in}(t,z)}$ is denoted $F_{in}(I,z)$ in the following to emphasize its dependence on I. This time average is taken over the random $f_1(t)$ and $f_2(t)$ distribution functions.

This separates the time average of the interaction Hamiltonian $\overline{\hat{H}_{in}(t)}=\hat{H}_{in}(I)$ (taken on a given τ time interval) from the average of the $f_1(t)f_2(t)$ time distribution. It comes directly for $\overline{F_{in}(t,z)}$ on a long observation interval Δt:

$$F_{in}(I,z)=\overline{f_1(t)f_2(t)}\langle\psi(z)|-\nabla_z\overline{\hat{H}_{in}(t)}|\psi(z)\rangle. \qquad (3)$$

In the following, we will use in Eq. (1) the time average version $F_{in}(I,z)$ of $F_{in}(t,z)$. Introducing the efficiency γ_{in} of the inelastic effect compared to the elastic events, $\overline{f_1(t)f_2(t)}=\gamma_{in}\tau/T$,[28] using the Hellmann-Feynman theorem, and introducing I instead of T in Eq. (3) it comes directly from Eq. (3):

$$F_{in}(I,z)=-\gamma_{in}\tau\frac{I(z)}{e}\nabla_z[\langle\psi(z)|\hat{H}_{in}(I)|\psi(z)\rangle]. \qquad (4)$$

III. TIME-AVERAGED INELASTIC INTERACTION HAMILTONIAN

In the duration τ of an inelastic event, the $\hat{H}_{in}(t)$ Hamiltonian written in the Heisenberg representation can be expressed using a generalization of the Fröhlish electron-phonon coupling Hamiltonian:[26,29,30]

$$\hat{H}_{in}(t)=\sum_{m}\sum_{p,q}a_p^*(t)a_q(t)g_{m_{pq}}\hat{z}_{m_{pq}}|\phi_p\rangle\langle\phi_q|. \qquad (5)$$

The electronic part of $\hat{H}_{in}(t)$ is expanded over the valence-bond-like states $|\phi_p\rangle$, whose time quantum superposition is given by the $a_p(t)$ coefficients. Each displacement operator $\hat{z}_{m_{pq}}$ corresponds to a reaction coordinate m associated with the nonadiabatical potential energy surface of the $|\phi_p\rangle$ and $|\phi_q\rangle$ time-dependent mixing. The corresponding vibronic coupling is given by the $g_{m_{pq}}$ constant. This is a linear term in view of the small $\Delta z_{m_{pq}}$ shift expected at a small I.

In Eq. (5), we only consider a transfer process from a monoelectronic state $|\phi_t\rangle$ (of the tip) towards a state $|\phi_s\rangle$ (of the surface) through one intermediate state $|\phi_a\rangle$ (of the adsorbate) which is very much out of resonance relative to $|\phi_t\rangle$ and $|\phi_s\rangle$. The most active term in Eq. (4) corresponds to an exchange of energy between the transferred electron and the z vibrational mode of the Xe surface energy potential well. The corresponding $a_a(t)$ coefficients can be obtained inside each τ interval for $t \ll e/I$ by solving the time-dependent Schrödinger equation describing a single-electron transfer process from $|\phi_t\rangle$ to $|\phi_s\rangle$ via $|\phi_a\rangle$. The oscillating behavior of the $|\phi_a\rangle$ occupation amplitude is given by (see the Appendix)

$$a_a(t) = \sqrt{\frac{4(\alpha^2+\beta^2)}{a^2+4(\alpha^2+\beta^2)}} \sin\left(\frac{\sqrt{a^2+4(\alpha^2+\beta^2)}}{2\hbar} \right), \quad (6)$$

with $\alpha = \langle \phi_t | \hat{h} | \phi_a \rangle$, $\beta = \langle \phi_s | \hat{h} | \phi_a \rangle$ and $a = (\epsilon_t - \epsilon_a) = (\epsilon_s - \epsilon_a)$, where ϵ_t, ϵ_a, and ϵ_s are, respectively, the energies of the tip, adsorbate, and surface states, and $\hat{h}$ is the monoelectronic Hamiltonian of the system. Notice that for an electronic friction problem, a multielectronic description would have to be used here instead of a single monoelectronic level. To calculate $\hat{H}_{in}(I)$ on a given time interval τ, we have first evaluated the quantity $(1/\tau)\int_0^\tau |a_a(t)|^2 dt$ which is the average occupation probability of the virtual state $|\phi_a\rangle$ on a given time interval τ. This represents the time average of the inelastic interaction Hamiltonian during the electron transfer time $\tau = h/[-a + \sqrt{a^2+4(\alpha^2+\beta^2)}]$ (see the Appendix).

Let us insist on the fact that τ is not the residence time of a tunneling electron on a given virtual resonant adsorbate state as often supposed.[31,32] The transferred electrons are not in a ballisticlike field emission state but in a time-dependent superposition of states mixing up the tip and surface states with the adsorbate states. As in any through bond electron transfer processes, the virtual orbitals of the adsorbate supporting the tunneling process are never fully occupied by the tunneling electrons. It is the quantum state trajectory of this transfer process which is weakly deviated, outside the state space generated by the tip and the surface states, by the presence of the adsorbate states.Thus, at a given tunnel current intensity I, the expression of the time-averaged Hamiltonian corresponding to the inelastic interaction takes the following form:

$$\hat{H}_{in}(I) = \frac{\alpha^2+\beta^2}{a^2+4(\alpha^2+\beta^2)} g\hat{z} |\phi_a\rangle\langle\phi_a|. \quad (7)$$

In Eq. (7), g is the vibronic coupling term along the reaction coordinate z, and $\hat{z}$ is the corresponding displacement operator. Introducing the overlap integrals $\langle \phi_t | \phi_a \rangle$ and $\langle \phi_s | \phi_a \rangle$ of the state $|\phi_a\rangle$ with all the states of both the tip and the surface, one can average, around the adsorbate equilibrium position $z_0 = \sqrt{\hbar/2M\omega}$, over the electronic and vibrational states and the result is

$$\langle \hat{H}_{in}(I) \rangle (z) = \frac{1}{(1.75)^2} \frac{g}{a^2+4(\alpha^2+\beta^2)} \times \sqrt{\frac{\hbar}{2M\omega}} \frac{\alpha\beta(\alpha^2+\beta^2)}{a^2}, \quad (8)$$

where the product $\langle \phi_t | \phi_a \rangle \langle \phi_s | \phi_a \rangle = \alpha\beta/[(1.75)^2 a^2]$ has been expressed using the Wolfberg-Hellmost formula,[33] ω is the adsorbate vibrational frequency, and M is the reduced mass of the corresponding mechanical degree of freedom. For small electronic coupling between the electronic states $|\phi_t\rangle$ of the tip and $|\phi_s\rangle$ of the surface through the adsorbate states $|\phi_a\rangle$, the tunneling current intensity is given at small bias voltage V_{bias} by[34]

$$I(z) = \frac{e^2 V_{bias}}{\pi\hbar} |V_{ts}|^2 \rho_t \rho_s, \quad (9)$$

where the electronic effective coupling $|V_{ts}| = (\alpha^2+\beta^2)/2a$ has been calculated to the first order following the standard effective Hamiltonian technique used in electron transfer theory (see the Appendix). Calculating the density of states $\rho_t = \alpha/[\pi(a^2+4\alpha^2)]$ and $\rho_s = \beta/[\pi(a^2+4\beta^2)]$ as usual[31] and after some simplifications the result is

$$\langle \hat{H}_{in}(I) \rangle (z) = 0.33 \frac{\pi\hbar}{e^2 V_{bias}} \times \sqrt{\frac{\hbar}{2M\omega}} \frac{a^2}{(\alpha^2+\beta^2)} g I(z). \quad (10)$$

Finally, the full expression of the average inelastic force exerted on the Xe adsorbate used in Eq. (1) is given by

$$F_{in}(I,z) = -0.33 \gamma_{in} \tau \frac{I(z)}{e} \frac{\pi\hbar}{e^2 V_{bias}} \sqrt{\frac{\hbar}{2M\omega}} g \frac{d}{dz} \times \left(\frac{a^2}{\alpha^2+\beta^2} I(z) \right), \quad (11)$$

where for a given z_{tip}, α and β are dependent on z to the first order and a to the second order.

This expression contains the usual proportional dependence of the inelastic effect on the tunnel current intensity[7] which is measured by an ampermeter positioned away from the tunnel junction. The z derivative in Eq. (11) encompasses two well-known terms: the standard nonadiabatic coupling $da(z)/dz$ taken here without a linearization and the $dI(z)/dz$ term often considered as a second-order term[7] which recovers in Eq. (11) its full influence. Finally, Eq. (11) also contains explicitly the electronic characteristic of an electron transfer process because of the intratunnel barrier electronic coupling α and β which are also z dependent.

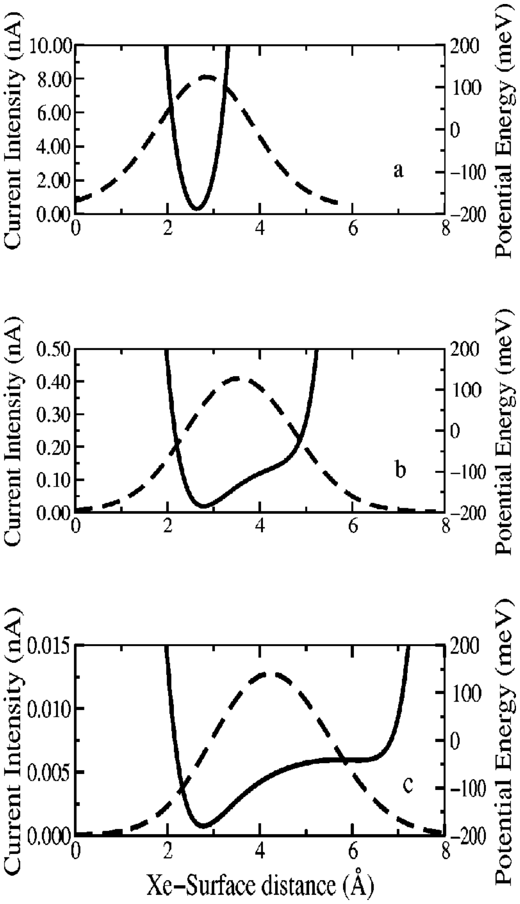

FIG. 3. Potential energy curves $U(z)$ (solid lines) and the tunnel current intensity $I(z)$ (dashed lines) as function of the Xe-surface distance z for $z_{tip}=6.0$, 8.0, and 10.0 Å from top to bottom.

IV. Xe POTENTIAL ENERGY AND CURRENT INTENSITY CURVES

The potential energy curves $U(z)$ and the current intensity functions $I(z)$ were calculated for tip-surface distances of 6.0, 8.0, and 10.0 Å using calculation techniques already described elsewhere[23] (see Figs. 1 and 3). The mesh parameter for Cu bulk is taken equal to 2.55 Å and the total interaction potential is estimated by superposition of the Cu-Cu and Cu-Xe pair potentials for a given tip-apex–metal-surface separation z_{tip} and for a given Xe atom position z including the N-body multipole interactions self-consistantly.[35] The current intensity curves are calculated using the electron scattering quantum chemistry (ESQC) technique.[36]

Figure 3 shows that the static potential energy curves minima are different compared with the tunnel current maxima position. The corresponding shifts are, respectively, 0.2, 0.8, and 1.5 Å. For a small z_{tip} value, the potential barrier disappears and the Xe atom is stabilized on the metal surface because of the deformation of the surface diffusion barrier introduced by the tip apex. In this case the apex creates a van der Walls trap for the Xe atom.[23] The double-well-like shape of $U(z)$ appears at very large z_{tip} distance corresponding to a too small I to induce Xe transfer from one well to the other. This rules out the standard interpretation of the transfer process currently in use in the literature.[32,37] This interpretation is based on the double-well potential model where the Xe atom is transferred from one well (the surface) to the other (the tip) due to a multiple excitation of the vibration levels of the Xe in the surface well. There is no need for such transition effects because at the experimental distance, the double-well potential is not completly formed for the Xe atom. From $z_{tip}=10.0$ Å to $z_{tip}=6.0$ Å the resistance of the tunnel junction, which is simply estimated by the quantity V_{bias}/I, decreases from 1.0 GΩ to 1.0 MΩ which is comparable to the experimental value of 0.906 MΩ where the Xe transfer experiments have been performed.[1]

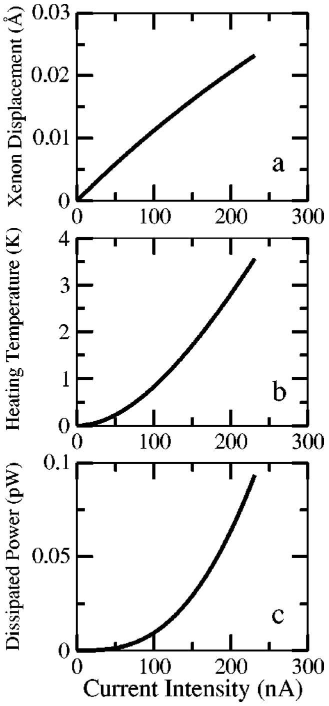

FIG. 4. (a) Xenon displacement Δz, (b) vibrational temperature T_{vib}, and (c) tunneling electrons dissipated power P_{diss}, as a function of the tunnel current intensity I for $z_{tip}=6.0$ Å.

V. RESULTS AND DISCUSSION

Many parameters are required to solve Eq. (1) with Eq. (11): γ_{in}, g, a, α, and β. From ESQC, we found $a=5.0$ eV, $\alpha=0.2$ eV, and $\beta=0.6$ eV.[32,38] For Xe, only g and γ_{in} remain noncalculable at present. γ_{in} can be evaluated experimentally by performing a large number of adsorbate extractions.[32] The resulting statistic is fitted by a Boltzmann law which gives $\gamma_{in}=6.6\times10^{-4}$. A few g are known like 4.1 eV/Å for the $2\pi^*$ carbon-carbon bond in trans-polyacetylene,[29] 10.0 eV/Å for the $2\pi^*$-CO bond on a metal surface.[37] We have taken $g=2.29$ eV/Å for the 6s state of a Xe atoms adsorbed on a Cu(110) surface.[32] With those parameters values, the maximum electronic population $|a_a(t)|^2$ of the state 6s is only 6.0×10^{-3}.

The calculated Xe Δz permanent displacement compared to its $I=0$ static equilibrium position is presented in Fig. 4(a) as a function of I. Here Δz results from competition between

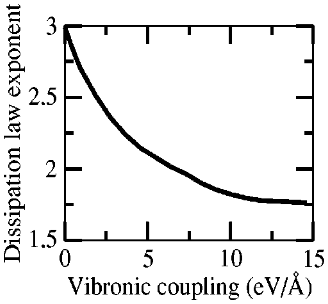

FIG. 5. Variation of the exponent λ of the dissipated power fitted law as a function of the vibronic coupling coefficient g for $z_{tip}=6.0$ Å.

the static $-\nabla U(z)$ which drives Xe towards its equilibrium position and $F_{in}(I,z)$ which forces the Xe atom in the STM junction to reach a z altitude corresponding to the maximum possible current accessible for the STM junction at a given z_{tip} (see Fig. 3). The STM junction is driven by the inelastic force towards the maximum possible I by the Xe Δz shift against the surface attractive force. An equivalent Xe heating temperature $T_{vib}(I)$ can be defined by simply calculating the $U(z)$ increase corresponding to a given Δz as presented also in Fig. 4(b). This temperature is a little below the usually estimated Xe transfer temperature from surface to tip.[37] The dependence of the vibrational temperature on the tunnel current can be fitted by a function in the form $T_{vib}=a_0+a_1 I^{\sigma}$, in where T_{vib} is expressed in K and I in nA, with $a_0=0$ K the temperature of the surface, $a_1=12.2\times 10^{-4}$, and $\sigma=1.37$.

After the transitory regime, a permanent Δz shift is maintained at a given I due to the energy released by the tunneling electrons on the z Xe degree of freedom. On average, the inelastic force $F_{in}(I,z)$ is active each time interval $e(\gamma_{in} I)^{-1}$ which leads to a dissipated power $P_{diss}(I)=F_{in}(I,z)\Delta z(I)\gamma_{in} I/e$. As shown in Fig. 4(c), $P_{diss}(I)\propto I^{\lambda}$ with $\lambda=\lambda(g)$ and remains very small. For example, $I=100$ nA leads to $P_{diss}=0.08$ pW, while the overall power dissipation in an STM junction is $P=RI^2=10$ nW for a junction resistance of $R=1$ MΩ. The variation of the exponent λ as function of g is given in Fig. 5. For small g, $\Delta z(I)$ do not saturate at large I and $\lambda>2$ because, from Eq. (10), $F_{in}(I,z)$ is at least proportional to I. On the contrary, for large g, $\Delta z(I)$ saturates and therefore $\lambda<2$.

VI. CONCLUDING REMARKS

The small amount of energy released by the tunneling electrons on a single adsorbate have been calculated in a semiclassical approach. An individual electron transfer event through an intermediate state is usually represented by an almost periodic trajectory on the Hilbert-state space. The dissipation process involved in our calculation models the deviation of this trajectory induced by a vibrational manifold in interaction with this intermediate state. This deviation is due to a small dilution of the wave paquet representing the transferred electron on this manifold. This intermediate state is almost not occupied but enough for this dilution to progressively accumulate energy in the vibrational manifold. This leads to an apparent Δz shift of the adsorbate position. This approach can be extended to describe inelastic tunnel processes in large molecules for the design of moleculars machines driven by a tunnel current.

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APPENDIX

To obtain an analytical expression for the time occupation amplitudes $a_a(t)$ introduced in Sec. III, the time-dependent Schrödinger equation was solved for the simple three-level system $\{\phi_p\}=\{|\phi_t\rangle,|\phi_a\rangle,|\phi_s\rangle\}$ with the monoelectronic effective Hamiltonian

$$H=\begin{bmatrix}\epsilon_t & \alpha & 0\\ \alpha & \epsilon_a & \beta\\ 0 & \beta & \epsilon_s\end{bmatrix}.$$

When this three-level system is prepared in the nonstationary state $|\psi(t=0)\rangle=|\phi_t\rangle$, we obtain

$$|a_s(t)|^2=\left(\frac{\alpha\beta}{\alpha^2+\beta^2}\right)\left\{\left(\frac{x}{X}\cos\frac{Xt}{2\hbar}-\cos\frac{xt}{2\hbar}\right)^2-\left(\sin\frac{Xt}{2\hbar}-\sin\frac{xt}{2\hbar}\right)^2+\left(1-\cos\frac{xt}{\hbar}\right)\right\},$$

$$|a_a(t)|^2=\frac{4(\alpha^2+\beta^2)}{X^2}\sin^2\frac{Xt}{2\hbar},$$

$$|a_t(t)|^2=1-|a_a(t)|^2-|a_s(t)|^2,$$

with $x=(\epsilon_a-\epsilon_t)$ and $X=\sqrt{(\epsilon_a-\epsilon_t)^2+4(\alpha^2+\beta^2)}$.

To evaluate the electronic effective coupling V_{ts} between the tip state $|\phi_t\rangle$ and the surface state $|\phi_s\rangle$ through the adsorbate intermediate states $|\phi_a\rangle$, an effective Bloch Hamiltonian was built.[39,40] The effective Hamiltonian technique consists in projecting the eigenstates of H onto model space only defined by the $\{|\phi_t\rangle,|\phi_s\rangle\}$ basis set. The corresponding projector is $P=|\phi_t\rangle\langle\phi_t|+|\phi_s\rangle\langle\phi_s|$ and the Bloch effective Hamiltonian is written $H_{eff}=PUHU^{-1}P$, where U is a unitary transform which diagonalizes H in the complete space generated by the full basis set. The resulting H_{eff} matrix elements are.[39]

$$V_{tt}=\langle\phi_t|H_{eff}|\phi_t\rangle=\frac{1}{\Delta}(c_{tt}c_{ss}E_1-c_{ts}c_{st}E_2),$$

$$V_{st}=\langle\phi_s|H_{eff}|\phi_t\rangle=\frac{1}{\Delta}c_{ss}c_{ts}(E_1-E_2),$$

$$V_{ss}=\langle\phi_s|H_{eff}|\phi_s\rangle=\frac{1}{\Delta}(c_{ss}c_{tt}E_2-c_{st}c_{ts}E_1),$$

with $\Delta=c_{tt}c_{ss}-c_{ts}c_{st}$, the c_{pq} are the coordinates of the eigenvectors $|\psi_q\rangle$ of H, and the E_q are the corresponding eigenvalues, so that

$$|\psi_1\rangle=\frac{\beta}{\sqrt{(\alpha^2+\beta^2)}}|\phi_t\rangle-\frac{\alpha}{\sqrt{(\alpha^2+\beta^2)}}|\phi_s\rangle,$$

$$|\psi_2\rangle=\frac{X}{\sqrt{(\epsilon_t-E_2)+(\alpha^2+\beta^2}}\left(-\alpha/X|\phi_t\rangle+|\phi_a\rangle-\frac{\beta}{X}|\phi_s\rangle\right),$$

$$|\psi_3\rangle=\frac{X}{\sqrt{(\epsilon_t-E_3)+(\alpha^2+\beta^2)}}\left(\frac{\alpha}{X}|\phi_t\rangle+|\phi_a\rangle+\frac{\beta}{X}|\phi_s\rangle\right),$$

and $E_1=\epsilon_t$, $E_2=\epsilon_t+\frac{1}{2}(\epsilon_a+X)$, and $E_3=\epsilon_s-\frac{1}{2}(\epsilon_a+X)$.

Finally, by replacing the expressions of $|\psi_q\rangle$ coefficients on the $\{\phi_p\}$ basis set in the H_{eff} matrix elements it becomes

$$V_{tt}=\frac{\beta^2E_1+\alpha^2E_2}{\alpha^2+\beta^2},$$

$$V_{ts}=V_{st}=\frac{\alpha\beta(E_2-E_1)}{\alpha^2+\beta^2},$$

$$V_{ss}=\frac{\alpha^2E_1+\beta^2E_2}{\alpha^2+\beta^2}.$$

The effective electron transfer rate $k_{eff}=\tau^{-1}$ between $|\phi_t\rangle$ and $|\phi_s\rangle$ is calculated using the Rabi formula[27,39] which gives the oscillation frequency between the two $|\phi_t\rangle$ and $|\phi_s\rangle$ states coupled by the intermediate $|\phi_a\rangle$ state:

$$\tau^{-1}=\frac{1}{\pi\hbar}\{|V_{tt}-V_{ss}|+\sqrt{(V_{tt}-V_{ss})^2+4|V_{ts}|^2}\}.$$

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