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Possibility of coherent multiple excitation in atom transfer with a scanning tunneling microscope

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We examine atom transfer resulting from coherent multiple excitation of the adsorbate-substrate bond caused by inelastic tunneling of a single electron (or hole) via a negative- (or positive-) ion resonance. At low biases and in particular for the transitions resulting in atom transfer, the rates of coherent multiple excitation are nonlinear and also highly asymmetrical with respect to the polarity of the bias. We establish a simple criterion for the regime in which this mechanism dominates over earlier proposed mechanisms for atom transfer resulting from vibrational heating by sequential (incoherent) inelastic resonance tunneling. In the case of the atomic switch, where a Xe atom is transferred between a Ni surface and a tip, the vibrational heating mechanism is found to dominate over the coherent mechanism. For other systems, such as Na adsorption on Cu or O_2 adsorbed on Pt, the coherent mechanism is argued to play a role in bond breaking.

I. INTRODUCTION

In the past few years there have been very exciting developments in the ability to control the motion of individual atoms and molecules at surfaces on an atomic scale with the tip of a scanning tunneling microscope (STM).[1] Examples of such experiments, which involve the breaking and making of selected bonds, are desorption,[2,3] dissociation,[4] and reversible atom transfer[5,6] between the sample and the tip by the application of voltage pulses. At this stage different mechanisms for these processes, in particular for the atom transfer, are still being proposed and explored. The atom transfer is viewed as a potential barrier crossing problem between the potential wells formed by the attraction of the atom to the tip and the sample. The crossing of such a voltage-dependent barrier by thermal activation has been invoked in explaining the observed behavior of the transfer of a Si atom between a tungsten tip and a Si surface.[7] Nonthermal atom transfer processes, like single-atom tunneling[8] and vibrational heating by inelastic electron tunneling,[9,10] have been put forward in explaining the power-law dependence observed by Eigler, Lutz, and Rudge[6] of the transfer rate of a Xe atom between a Ni surface and a tungsten tip as a function of applied voltage at cryogenic temperatures. In reality, a combination of tunneling and vibrational heating processes will be relevant, but the tunneling requires a small and narrow energy barrier and will therefore in most cases be important close to the top of the barrier. The common key feature of the proposed models for atom transfer via vibrational heating by inelastic electron tunneling is that they involve a stepwise vibrational excitation of the adsorbate-substrate bond, resulting in a strong nonlinear dependence of the transfer rate on the applied voltage.

The possibility of overcoming a potential barrier via excitations by inelastic electron scattering has also been stressed in connection with desorption induced by electronic transitions (DIET) (Ref. 11) and desorption driven by laser-excited hot electrons.[12] A key ingredient in this context is the nonadiabatic coupling between the ion cores and the electrons via an adsorbate-induced resonance. A prime example of such a resonance is the negative-ion resonance that is created when an affinity level of an atom or the lowest unoccupied molecular orbital (LUMO) of a molecule[13] is occupied. The electron, created in the substrate by absorption of a photon or coming from an incident electron beam, is temporarily trapped in such a negative-ion resonance state. While the electron is trapped in this state, the adsorbate wave packet resides on an excited-state potential energy surface and evolves in time until the resonance decays. The wave packet then returns to the ground-state potential energy surface, where it is now no longer exclusively in the lowest vibrational state. In fact, it is possible that the adsorbate escapes by ending up in a state above the barrier, which results in the fission of the adsorbate-substrate bond. On a strictly repulsive excited-state potential energy surface, and in the case of a long-lived resonance, the bond can also be broken if a part of the wave packet escapes before it returns to the ground-state potential, resulting in a negative ion. Even if the adsorbate ends up in a vibrationally excited state below the barrier there is a chance of crossing the barrier at a later time

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by additional transitions created by the transient trapping of subsequent electrons in the resonance state. This process, refered to as the desorption induced by multiple electronic transitions (DIMET) mechanism,[14] requires that the excited-vibrational-state lifetimes are not too short compared to the average time between subsequent electron scattering events. This mechanism, where the multistep vibrational excitation is created by many single steps, is completely analogous to the proposed vibrational heating mechanism for atom transfer in STM, while a mechanism analogous to the above DIET process for bond breaking via a multistep vibrational excitation in a single jump has not so far been discussed in detail for atom transfer. This latter mechanism is in this work referred to as atom transfer by multiple *coherent* excitation, as opposed to the vibrational heating mechanism by inelastic tunneling, which is referred to as transfer induced by multiple *incoherent* excitations.

In this paper, we explore and discuss the atom transfer resulting from multiple vibrational excitations of the adsorbate-substrate bond caused by inelastic tunneling of a single electron via an adsorbate-induced resonance level. Our analysis is based on a simple resonance level model and a truncated oscillator model for atom transfer, as in Ref. 9. This inelastic resonance tunneling model is closely related to the model used in the description of DIET.[15] Multiple coherent excitations can also take place by dipole coupling, but in this work we focus on the resonance coupling, since the experience gained from treatments of electron-hole pair damping of adsorbate vibrations[16] and vibrational excitation by inelastic electron tunneling[17] suggests that this resonance coupling is often dominant. We consider only the situation of a negative- or positive-ion resonance where the occupancy of the resonance level is nearly empty or full. For instance, despite the fact that the resonance derived from the 6s valence level of a Xe atom adsorbed on a Ni surface is located well above the Fermi level, it has been argued that it gives a dominant contribution to the tunneling current.[18]

A characteristic feature of the STM that we will exploit in this work is that the occupancy of the resonance by the tunneling electrons and the corresponding inelastic coupling can be controlled by varying the magnitude and polarity of the applied voltage. While the overall current is directly related to the occupancy of the resonance, as controlled by the bias, the rates of vibrational excitations are more complicated and depend also on the force experienced by the atom on the excited-state potential energy surface, on the width of the resonance, and on the energies of the tunneling electrons relative to the center of the resonance. We find that, at low biases, the rate of transfer as a result of coherent multiple excitation will be proportional to the bias, but that it quickly becomes nonlinear, and that this nonlinearity is more pronounced for excitations to higher-lying vibrational levels. We also establish that the polarity of the bias required to cause transfer depends on whether the resonance is nearly empty or full. We compare the relative efficiency of coherent and incoherent multiple excitation with respect to atom transfer and establish that the key factor is the magnitude of the tunneling particle current through the resonance relative to the inverse vibrational lifetime. For instance, in the case of reversible Xe atom transfer between a Ni surface and the tungsten tip, the relatively long vibrational lifetime suggests that the incoherent multiple excitation mechanism dominates over the coherent one, whereas for other systems, e.g., Na adsorbed on Cu(111) or O_2 adsorbed on Pt(111), where the vibrational lifetime is expected to be significantly shorter, the coherent multiple excitation mechanism can play a significant role in the bond breaking.

After presenting our model for atom transfer by coherent multiple excitation in Sec. II, the necessary theory for the calculation of the transfer rate is developed in Sec. III. The resulting dependence of the multiple excitation and transfer rate on the resonance parameters is presented and discussed in Sec. IV. In addition, the criteria for the relative roles of coherent and incoherent multiple excitation in atom transfer are presented, and used in the discussion of the observed reversible Xe transfer between a Ni surface and a W tip. Here we also speculate about the possibility of Na atom transfer between a Cu(111) surface and a tip and intramolecular bond breaking of the O_2 molecule adsorbed on Pt(111). Finally, Sec. V contains some concluding remarks.

II. MODEL

We adopt the same model for the electronic structure of the adsorbate, the tip, and the sample as used previously in the description of Xe transfer on Ni(110).[9] Related resonance models including a coupling to a local oscillator have appeared in many different contexts as stressed by Gadzuk[15] and are often referred to as local polaron models. Thus it seems only necessary to give a summary of this model here.

The adsorbate-induced resonance is modeled by a single orbital with an energy ϵ_a interacting with two continua of electron levels representing the tip and the sample, respectively, as shown in Fig. 1. The applied voltage V between the tip and the sample is represented by a shift eV of their Fermi levels with respect to each other. In order to cover both directions of atom transfer, i.e., from

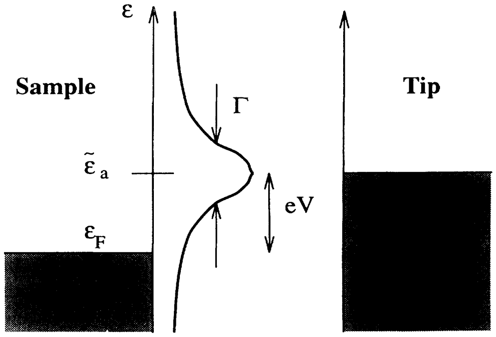

FIG. 1. Model of the electronic structure of the tip-sample system, with an atom adsorbed on the sample.

the sample to the tip and vice versa, the bias V is defined as the electrostatic potential difference between the electrode on which the atom is initially adsorbed and the electrode to which the atom is transferred. The adsorbate level turns into a resonance due to the interaction with the two continua of levels. For simplicity, this resonance, centered around an energy $\tilde{\epsilon}_a$, is assumed to have a Lorentzian line shape with a full width at half maximum Γ. We assume that $\tilde{\epsilon}_a$ is fixed with respect to the Fermi level ϵ_F of the tip or the sample on which the adsorbate is located (as is taken for granted in Fig. 1). The width $\Gamma = \Gamma_s + \Gamma_t$ has contributions from the partial widths Γ_s and Γ_t due to the interaction with the sample and tip, respectively. Typically, the partial width from the electrode on which the adsorbate is located dominates. We will only deal with the cases of a negative- or a positive-ion resonance. In the case of a negative-ion resonance, $\tilde{\epsilon}_a$ is well above the Fermi level ϵ_F (compared with Γ) and has an average occupancy $n_a \ll 1$, whereas in the case of the positive-ion resonance $\epsilon_F - \tilde{\epsilon}_a \gg \Gamma$ and $1 - n_a \ll 1$. The situation of a partially occupied resonance, where $\tilde{\epsilon}_a$ is close to ϵ_F compared to Γ is a very interesting one but requires a different approach. The spin is simply included in our treatment by an extra factor of 2 at the appropriate places.

The atom transfer rate will be calculated and discussed using a truncated oscillator model.[19] This means that the ground-state potential energy surface $V_0(z)$ for the adsorbate is assumed to be harmonic and that the continuum of levels above the barrier is represented by the discrete levels of $V_0(z)$ with energies above the barrier, as shown in Fig. 2. The modeling of the nonadiabatic coupling between the adsorbate ion cores and the resonant level is done in a standard manner by assuming that ϵ_a shifts linearly with the adsorbate coordinate z; $\epsilon_a(z) = \epsilon_a + z\partial\epsilon_a/\partial z$. In the case of a negative-ion resonance, the excited-state potential energy curve $V^*(z)$ is given by $V^*(z) = V_0(z) - Fz$, where $F = -\partial\epsilon_a/\partial z$ is the force, while for a positive-ion resonance the excited-state potential energy curve is given by $V^*(z) = V_0(z) + Fz$. In both cases $V^*(z)$ is simply a displaced version of $V_0(z)$. The neglect of the change in curvature between $V^*(z)$ and $V_0(z)$ is vindicated by the fact that the resonance lifetime on metal surfaces is typically much shorter than the vibrational period, corresponding to an impulsive collision. While the electron is trapped in such a short-lived resonance state, the displacement of the adsorbate wave packet on $V^*(z)$ (but not the change in its momentum) can be neglected.

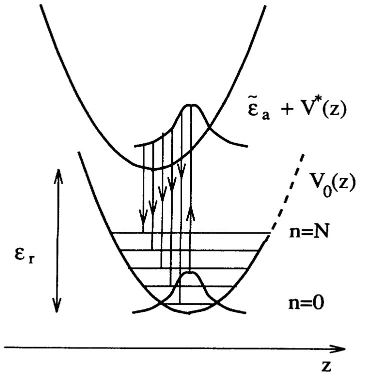

FIG. 2. Potential energy curves and evolution of the wave packet in the truncated oscillator model.

III. THEORY

Since our model for atom transfer based on the multiple coherent excitation mechanism is closely related to the model for DIET developed by Gadzuk,[15] we will simply use the results compiled in this work to derive explicit expressions for the rate of coherent multiple vibrational excitation by inelastic electron tunneling in the impulse limit, and apply these to the calculation of the rate of transfer. We will develop the theory for a negative-ion resonance and indicate at appropriate places how a positive-ion resonance can be treated by considering scattering of holes instead of electrons.

We start with a well-known result from the literature that has been nicely discussed by Gadzuk,[15] for the probability, $P_n(\epsilon_i)d\epsilon_i$, that an electron scattering through the resonance with incident energy ϵ_i causes a vibrational transition from the ground state ($n = 0$) to the nth excited state,

$$P_n(\epsilon_i)d\epsilon_i = \frac{\Gamma}{2\pi}\left|\sum_{m=0}^{\infty}\frac{\langle n|\tilde{m}\rangle\langle\tilde{m}|0\rangle}{(\epsilon_r - \epsilon_i) + m\hbar\omega_0 - i\Gamma/2}\right|^2 d\epsilon_i\,, \quad (1)$$

where the $|\tilde{m}\rangle$ are the vibrational states on $V^*(z)$, ω_0 the vibrational frequency in the excited- (and also the ground-) state potential well of the adsorbate with mass μ, and $\epsilon_r[= \tilde{\epsilon_a} - F^2/(2\mu\omega_0^2)]$ is the energy of the center of the resonance which includes a relaxation shift for the adsorbate on $V^*(z)$. In the case of a positive-ion resonance, $P_n(\epsilon_i)d\epsilon_i$ is viewed as the scattering probability for a hole, with an energy $\epsilon_F - \epsilon_i$ relative to ϵ_F, in an electron state with an energy ϵ_i below ϵ_F. The expression for $P_n(\epsilon_i)$ in (1) can be evaluated in two ways; the method that follows, in the time domain, has the advantage that it is easier to relate to the discussion of excitation that we presented above. The alternative method (discussed in the Appendix) is however more general, in that it is more easily applicable to the case of excitation between any two levels; the treatment below applies only to the case of excitation to or from the ground state.

The time-dependent method is based on converting the summation in (1) into a time integral,

$$P_n(\epsilon_i) = \tfrac{\Gamma}{2\pi\hbar^2}\left|\int_0^{\infty}\langle n|e^{-iH^*\tau/\hbar}|0\rangle \right.$$
$$\left. \times\ e^{-i(\epsilon_i-\epsilon_r)\tau/\hbar}e^{-\Gamma\tau/2\hbar}d\tau\right|^2, \quad (2)$$

where $H^* = \sum_{m=0}^{\infty}\hbar\omega m|\tilde{m}\rangle\langle\tilde{m}|$ is the Hamiltonian for the adsorbate on $V^*(z)$, excluding the zero-point energy $\hbar\omega_0/2$ and the relaxation shift. This expression for $P_n(\epsilon_i)$ has a simple interpretation; it is the modulus squared of a time integral of the amplitudes for finding the electron in the resonance state and the wave packet in a vibrationally excited state n of $V_0(z)$ after propagation on $V^*(z)$. In the evaluation of Eq. (2), we will be concerned with the short-time limit, obtained when the dominant contribution to the time integral comes from $\tau \ll \omega_0$. This condition is fulfilled either when $\Gamma/2 \gg \omega_0$ or $|\epsilon_i - \epsilon_r| \gg \omega_0$ or, more generally, whenever $\Gamma_{\rm eff} \gg \omega_0$, where $\Gamma_{\rm eff}$ is an effective energy-dependent width defined by

$$\Gamma_{\rm eff} = [(\epsilon_i - \epsilon_r)^2 + \Gamma^2/4]^{1/2} \, . \tag{3}$$

In this short-time limit, the value of the matrix element in (2) is given by the standard result,[20]

$$\langle n|e^{-iH^*\tau/\hbar}|0\rangle = e^{-(\lambda\omega_0\tau)^2/2}(\lambda\omega_0\tau)^n/\sqrt{n!} \, , \tag{4}$$

where λ is a dimensionless coupling constant which relates to the force on the adsorbate in $V^*(z)$ according to $\lambda = F/(2\mu\hbar\omega_0^3)^{1/2}$. Note that the probabilities corresponding to the amplitudes for the different values of n form a Poisson distribution. In the evaluation of the time integral in (2) using (4), we will make use of a somewhat more restrictive definition of the impulsive limit as $n\lambda\hbar\omega/\Gamma_{\rm eff} \ll 1$. The term $e^{-(\lambda\omega\tau)^2/2}$ is then close to unity in the region near the maximum of the integrand, and can therefore be ignored. This leads to

$$P_n(\epsilon_i) \simeq \frac{n!\Gamma}{2\pi}\frac{(\lambda\hbar\omega_0)^{2n}}{[(\epsilon_r - \epsilon_i)^2 + \Gamma^2/4]^{n+1}} \, . \tag{5}$$

Note that this distribution is no longer a Poisson distribution, and the presence of the factor $n!$ leads this expression to break down for large n when $n \sim \Gamma_{\rm eff}/(\lambda\hbar\omega_0)$.

It is useful to understand the relation between the result for $P_n(\epsilon_i)$ in (5) and the standard DIET result.[21] The latter is obtained by determining the occupation P_n of a level n on the assumption that the resonance-state lifetime has a single value, and then integrating this over an exponential distribution of lifetimes,

$$P_n = \frac{\Gamma}{\hbar}\int_0^\infty |\langle n|e^{-iH^*\tau/\hbar}|0\rangle|^2 e^{-\Gamma\tau/\hbar} d\tau. \tag{6}$$

This expression is nothing other than an average over the distribution of resonance lifetimes of probabilities of finding the wave packet on $V^*(z)$ in a vibrationally excited state n of $V_0(z)$, as opposed to the integral of amplitudes in (2) . As noted by Gadzuk[15] the expression for P_n in (6) is obtained just by integrating $P_n(\epsilon_i)$ in (1) over all incident energies. Inserting the expression (4) for the matrix element, in the impulsive limit one arrives at

$$P_n \simeq \frac{2n!}{n!}\left(\frac{\lambda\hbar\omega_0}{\Gamma}\right)^{2n} \, . \tag{7}$$

Note that the impulsive limit corresponds to a weak inelastic coupling since P_n decays rapidly with n and $P_0 \simeq 1$. A similiar result to Eq. (7) is now obtained for the relative probabilities of excitation by a single electron,

$$\frac{P_n(\epsilon_i)}{P_0(\epsilon_i)} \simeq n!\left(\frac{\lambda\hbar\omega_0}{\Gamma_{\rm eff}}\right)^{2n} \, , \tag{8}$$

but now with Γ replaced by $\Gamma_{\rm eff}$ and a slightly different distribution over the levels. Note that the effective coupling constant $(\lambda\hbar\omega_0/\Gamma_{\rm eff})^2$ in (8) is equal to $\hbar F^2/(2\mu\omega_0\Gamma_{\rm eff}^2)$, which is nothing other than the strength parameter in a forced oscillator model description in the impulsive limit; the impulse is simply $F\hbar/\Gamma_{\rm eff}$, where $\hbar/\Gamma_{\rm eff}$ is interpreted as a collision duration time.

Now we turn to the application of the main result, Eq. (5), to the problem of atom transfer with the STM. We will do that by first determining I_n, the current causing a transition to level n. In order to calculate I_n we need to discuss some of the effects of the Pauli exclusion principle. In the situation of a biased tip such that $|eV|$ is larger than the excitation energy $n\hbar\omega_0$ there will always be an empty final state for the inelastically scattered electrons. Hence, we can adopt the expression for the total current I in the one-dimensional (zero-temperature) case, developed by Wingreen, Jacobsen, and Wilkins,[22]

$$|I| = \tfrac{2e}{\pi\hbar}\int_{\epsilon_{fF}}^{\infty} d\epsilon_f \int_{\epsilon_{fF}}^{\epsilon_{iF}} d\epsilon_i \frac{2\pi\Gamma_s\Gamma_t}{\Gamma} \times \sum_{n=0}^{\infty} P_n(\epsilon_i)\delta(\epsilon_i - \epsilon_f - n\hbar\omega), \tag{9}$$

where ϵ_f is the final energy of the electron. The final state of the electron is on the same electrode as the adsorbate when $V > 0$. For $V < 0$, the initial location of the electron is on this electrode. The Fermi levels ϵ_{iF} and ϵ_{fF} are associated with the electrodes on which the incident and the scattered electrons are located, respectively; $\epsilon_{iF} = \epsilon_F + eV$ and $\epsilon_{fF} = \epsilon_F$ when $V > 0$, and $\epsilon_{iF} = \epsilon_F$ and $\epsilon_{fF} = \epsilon_F + eV$ when $V < 0$. The current causing excitation to the nth level is then

$$I_n = \frac{4e\Gamma_s\Gamma_t}{\hbar\Gamma}\int_{\epsilon_F}^{\epsilon_F + eV} P_n(\epsilon)d\epsilon. \tag{10}$$

Note that the current is defined to be positive for positive V. In the situation of a positive-ion resonance $\tilde{\epsilon}_a < \epsilon_F$, we obtain, by considering scattering of holes instead of electrons, the same result as for a negative-ion resonance located $\epsilon_F - \tilde{\epsilon}_a$ above ϵ_F, if the polarity of V is reversed.

The rate of transfer to the nth level is now simply $|I_n/e|$. Consequently in the truncated harmonic oscillator,[19] if the potential well has N bound states, the rate of transfer $R^{\rm coh}$ to the tip is given by,

$$R^{\rm coh} = \sum_{n=N}^{\infty}\left|\frac{I_n}{e}\right| \, . \tag{11}$$

In the impulsive limit of interest here, the sum in Eq. (11) is dominated by its first term $|I_N/e|$ and $R^{\rm coh} \simeq |I_N/e|$. Finally, it is useful to note that an upper limit of $|I_n|$ is obtained by an integration over all ϵ in (10) and is given by,

$$I_n^{\rm max} = \frac{4e\Gamma_s\Gamma_t}{\hbar\Gamma}P_n, \tag{12}$$

where P_n is defined in Eq. (6). In the next section, we will use this result to separate out the coupling strength λ when presenting the results for I_n.

IV. RESULTS AND DISCUSSION

In this section we aim to present our results in such a way that they are not only applicable to a specific system like Xe on Ni(110) but also to other adsorption systems where we have a negative- (or positive-) ion resonance close to the Fermi level. At the end we will discuss a few explicit systems in connection with the criteria established concerning the relative roles of coherent and incoherent multiple excitations. We will primarily discuss the case of a negative-ion resonance since the results for a negative- and positive-ion resonance are simply related to each other.

Parameters that are likely to vary between one system and another are the force F on the adsorbate on its excited-state potential energy surface, the width Γ of the resonance, and its position ϵ_r with respect to the Fermi level ϵ_F. The dependence of the transition rates I_n on the force F is separated out by normalizing against $I_n^{\max}$. The dependence on the two parameters Γ and $(\epsilon_r - \epsilon_f)$ is revealed by presenting results as a function of bias V against Γ or $(\epsilon_r - \epsilon_f)$ for a range of values of $|\epsilon_r - \epsilon_f|/\Gamma \gg 1/2$ appropriate for a negative- (or positive-) ion resonance.

The dependence of the elastic tunneling currents on the resonance parameters and the bias is shown in Fig. 3. Note that $I_0/I_0^{\max}$ depends on $(\epsilon_r - \epsilon_F)/\Gamma$ in a simple manner; the curve simply shifts rigidly with the parameter $(\epsilon_r - \epsilon_F)/\Gamma$ in such a way that the currents are all zero at zero bias and the inflection point occurs at $eV = \epsilon_r - \epsilon_F$. In particular, the sharp increase of I_0 with bias V at the inflection point arises because $P_0(\epsilon_i)$ has its maximum at $\epsilon_i = \epsilon_F$, corresponding to the maximum in the final density of states. The effect of Γ is just to determine the rate of this increase. Note also that the absolute magnitude of I_0 is highly asymmetric with respect to V. The same results are obtained for a positive-ion resonance simply by reversing the sign of V. For instance, the absolute magnitude of I_0 attains its largest values for negative V instead of positive V.

The behavior of the inelastic tunneling currents which cause transitions to different vibrational levels is illustrated in Fig. 4, for a negative-ion resonance, by comparing the currents for $n = 0$ and $n = 4$. It is sufficient to consider only a single value of $(\epsilon_r - \epsilon_F)/\Gamma$ since, according to Eqs. (5) and (10), the currents $I_n/I_n^{\max}$ just shift rigidly with $(\epsilon_r - \epsilon_F)/\Gamma$, in an analogous way to the elastic current ($n = 0$) as discussed above. The most important difference between I_4 and I_0 is the much more rapid increase with V of I_4 than I_0. This is simply because $P_n(\epsilon_i)$ goes to the $(2n+2)$th power of $\Gamma_{\text{eff}}(\epsilon_i)$ which makes the maximum of $P_n(\epsilon_i)$ increasingly more narrow for larger n. As a consequence, one expects that I_n and the corresponding transition rates to the nth level will depend nonlinearly on V.

A central result of this work is the nonlinear dependence of I_n on V in the tail of the resonance, as in Fig. 5. In this situation $\Gamma_{\text{eff}}(\epsilon_i) \simeq (\epsilon_r - \epsilon_i)$, the energy dependence of $P_n(\epsilon_i)$ is independent of Γ, and by normalizing V to $\epsilon_r - \epsilon_F$ instead of Γ it is sufficient to consider only a single value for $(\epsilon_r - \epsilon_F)/\Gamma$. The deviation of I_n from linear behavior for different n with respect to V is nicely illustrated by normalizing I_n to $(\Gamma/e)\frac{\partial I_n}{\partial V}(V = 0)$. The elastic current I_0 shows a near-linear behavior in a relatively large range of V while I_4 starts to deviate even at $|eV/(\epsilon_r - \epsilon_F)| \sim 0.05$. Since $P_n(\epsilon_i)$ goes essentially to the $(2n + 2)$th power of $(\epsilon_r - \epsilon_i)$ in the resonance tail, this behavior is no surprise and shows that the degree of nonlinearity increases rapidly with n. In fact, from Eq.

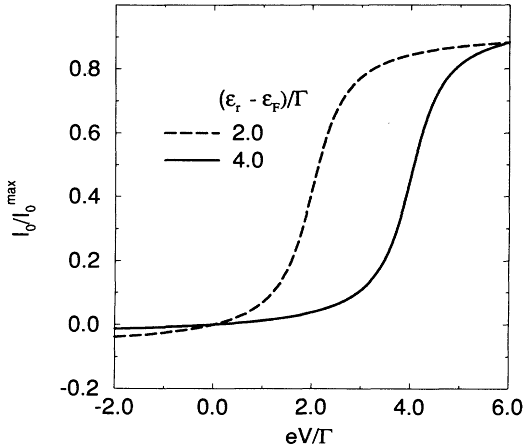

FIG. 3. Elastic tunneling current I_0 for different negative-ion resonance parameters. The current is normalized to its absolute maximum value $I_0^{\max}$ and is plotted against the applied bias eV normalized to the resonance width Γ for two different values of $(\epsilon_r - \epsilon_F)/\Gamma$. The results for a positive-ion resonance are simply obtained for the same absolute values of $(\epsilon_r - \epsilon_F)/\Gamma$ by reversing the polarity of V.

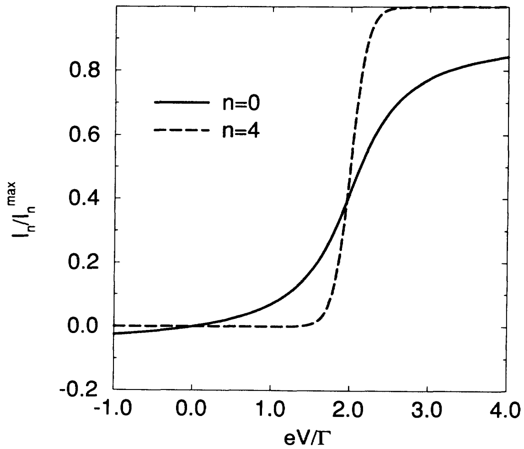

FIG. 4. Tunneling currents I_n causing transitions to different levels n for a negative-ion resonance. The currents are normalized to their absolute maximum values $I_n^{\max}$ and are plotted against eV normalized to the resonance width Γ for $n = 0$ and $n = 4$ with $(\epsilon_r - \epsilon_F)/\Gamma = 2$. The corresponding result for a positive-ion resonance is obtained by reversing the polarity of V.

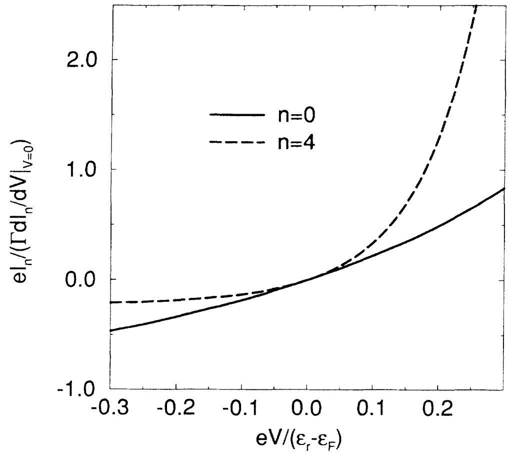

FIG. 5. Elastic and inelastic tunneling currents I_n in the tail of a resonance. The nonlinear dependence of the currents for $n = 0$ and $n = 4$ with $(\epsilon_r - \epsilon_F)/\Gamma = 2$ on the applied bias V is revealed by normalizing against the corresponding differential currents at zero bias. The bias eV has now been normalized to $(\epsilon_r - \epsilon_F)$, since in the resonance tail the functional dependence of the currents is no longer sensitive to Γ. The corresponding result for a positive-ion resonance is again obtained by reversing the polarity of V.

(10), $I_n/I_n^{\max}$ is given approximately by

$$\frac{I_n}{I_n^{\max}} \sim \frac{\Gamma^{2n+1}}{(\epsilon_r - \epsilon_F - eV)^{2n+1}} . \tag{13}$$

This result shows that the nonlinear dependence of I_n on V is not just a simple power law.

Having demonstrated the dependence of I_n on different resonance parameters we turn to a discussion of the possible implications for atom transfer. Recall that in the truncated harmonic oscillator model and in the impulsive limit, the rate of atom transfer R^{coh} is simply proportional to the tunneling current I_N causing transitions to a level N, where N is the number of levels in the ground-state potential well, which will vary from system to system. For instance, in the case of Xe on Ni(110), N has been argued to be 4 or 5. This example shows that a rather high multiple excitation might be needed for a transfer, and the transfer rate is not expected to be simply linear with bias V but to show a power-law dependence over a limited range of V. Hence, atom transfer by coherent as opposed to incoherent multiple excitations cannot simply be distinguished from the bias dependence. Another important effect is that R^{coh} is highly asymmetric with respect to the polarity of V. In the case of a negative-ion resonance where $\epsilon_r > \epsilon_F$, R^{coh} is much larger for positive V than for negative V, and conversely for a positive-ion resonance. This result is in contrast to atom transfer by incoherent multiple excitations, where the vibrational heating is more or less independent of the sign of V. However, in discussing the direction of transfer one should bear in mind that other effects, such as deformation of the potential well in the presence of an electric field, might influence or even mask the nonlinear dependence and the asymmetry of the transfer rate with respect to V. For instance, one source of well deformation is the interaction of the dipole moment of the adsorbed Xe atom with the electric field, making the well at the negative electrode shallower and thus favouring transfer towards the positive electrode.[8]

In order to decide if coherent multiple excitation plays an important role in atom transfer, it is necessary to explore in which regime (if any) this mechanism dominates over transfer by incoherent multiple excitations. An approximate expression for the transfer rate R^{incoh} via multiple incoherent excitation in the truncated oscillator model can easily be obtained as follows in the zero-temperature limit. A quasi-Boltzmann distribution is established over the levels populated by vibrational heating because of the competition between vibrational excitation by inelastic resonance electron scattering and deexcitation by creation of electron-hole pairs and phonons.[9,10] In the truncated harmonic oscillator model the rate of excitation from the $(n-1)$th level to the nth is given by $n|I_1/e|$, and $n\gamma$ is the corresponding rate of deexcitation. The probability of being in the nth level is therefore $|I_1/(e\gamma)|^n$. R^{incoh} is then simply the rate of transfer out of the $(N-1)$th level into the Nth level multiplied by the probability of being in the $(N-1)$th level,

$$R^{\mathrm{incoh}} \simeq (N-1)\left|\frac{I_1}{e}\right|\left(\frac{I_1}{e\gamma}\right)^{N-1} . \tag{14}$$

This should be contrasted with the rate of transfer $R^{\mathrm{coh}} \simeq |I_N/e|$ by *coherent* multiple excitation. At sufficiently low V, I_N depends linearly on V, and in this situation one obtains from Eqs. (10) and (5),

$$R^{\mathrm{coh}} \simeq N!\left|\frac{I_1}{e}\right|\left(\frac{I_1}{I_0}\right)^{N-1} . \tag{15}$$

A comparison between the two different results in (14) and (15) for the rates of transfer shows that coherent multiple excitation will dominate when sufficiently low currents flow through the resonance state, and the crossover to predominantly incoherent multiple excitations occurs at a current of about $I^* \approx ec_N\gamma$ where $c_N = [N!/(N-1)]^{1/(N-1)}$. Note that, as has already been stressed in connection with Eq. (7), the inelastic resonance scattering is weak so that the total current through the resonance is dominated by I_0. Surprisingly enough, this criterion does not change in any major way when the nonlinear dependence of I_n on V is taken into account, as can be seen from the result in (13). Finally, we note that this criterion is consistent with the implicit assumption behind the result for coherent multiple excitations in Eq. (10), namely, that the adsorbate vibration has time to relax to the ground state between the inelastic scattering events.

Atom transfer by coherent multiple excitation should be favored in situations where the vibrational relaxation rate γ is high or when the current is small. The vibrational relaxation rate γ shows a large variation over different systems. For instance, estimates of γ for Xe on

Ni(110) suggest that $\gamma \approx 3\times10^{10}\ \mathrm{s}^{-1}$ and is dominated by phonon damping.[23] Assuming that the dominant part of the current goes through the resonance, this corresponds to $I^* \approx 10$ nA and a bias of about 10 mV at the measured resistance of about 1 MΩ for the Xe switch. This argument suggests that for this system the rate of transfer by incoherent multiple excitations should dominate over the coherent one in the range 20–200 mV of V used in the experiment. However, the vibrational damping rate for this system is not particularly large, since the vibrational energy $\hbar\omega_0 \approx 4$ meV for the adsorbed Xe atom is low compared to the maximum phonon energy $\hbar\omega_{\max} \approx 37$ meV for Ni, which makes the phonon damping rate γ_{ph} relatively small.[23] Other systems exist where γ_{ph} can be about two orders of magnitudes larger. For instance, consider Na adsorption on Cu, which belongs to a most interesting class of adsorption systems with a negative-ion resonance. At low coverage, the Na adsorbate has an ionic character with a small occupancy of the resonance derived from the atomic 3s valence level; in addition, the observed vibrational frequency $\hbar\omega_0 \approx 21$ meV (Ref. 24) is relatively large compared to $\hbar\omega_{\max}(\approx 30$ meV). An adsorbate lattice-dynamics calculation[25] using the observed $\hbar\omega_0$ gives $\gamma_{\mathrm{ph}} \approx 8 \times 10^{12}$/s for Na adsorbed in a hollow site on Cu(111). This value for the relaxation rate corresponds to a crossover current I^* as high as 2 μA for $c_N \approx 2$. The remaining question is whether the other conditions that have to be met to obtain atom transfer can be fulfilled, e.g., whether the tip-surface resistance (and hence distance) is sufficiently high so that voltage is sufficiently large at these currents to give an appreciable transfer rate. For instance, the tip-surface distance employed is constrained by the need to ensure that the barrier formed between the tip and the sample is smaller than the diffusion barrier along the surface.

We end this section with a consideration of another potentially interesting system, O_2 adsorbed on Pt(111). Here one can imagine the possibility of studying not only molecule transfer but also the breaking of the internal molecular bond. Recent laser irradiation experiments have shown that it is possible to desorb or dissociate this adsorbed molecule with photoexcited hot electrons, either via a DIET mechanism using continous wave irradiation or by a DIMET mechanism using an intense femtosecond laser pulse.[26] We will here discuss the possibility of dissocating the adsorbed molecule using the tunneling current. At T∼80 K the oxygen molecule chemisorbs on Pt(111) in a molecular state characterized by electron-energy-loss spectroscopy EELS (Refs. 27 and 28) as having an internal vibrational frequency of 108 meV. The activation energy for dissociation has been estimated from the same measurements to be about 0.5 eV and a simple truncated oscillator model description of the dissociation gives N=5 or 6. The observed asymmetry of the vibrational line shape suggests that the damping rate is dominated by electron-hole pairs and the observed broadening would then yield $\gamma \sim 4 \times 10^{12}$/s.[29] Such a large value is not entirely unexpected in view of the participation of the antibonding π^* orbitals in the chemisorption bond, as evidenced not only by the large decrease of the internal stretch frequency upon adsorption, but also by the large dynamic dipole moment observed for this mode. The suggested value for γ corresponds to a relatively large value of about 1 μA for the crossover current I^* between the regimes of coherent and incoherent multiple excitations. Since the bond breaking in this situation does not involve formation of a barrier between tip and sample, it should be possible to vary the tunneling current over a wider range than for atom (or molecule) transfer and to investigate the different regimes of bond breaking by coherent or incoherent multiple excitations. One important consequence of a relatively large γ_{eh}, which is four orders of magnitude larger than for Xe on Ni, is that it should result in a relatively large dissociation rate. For this system there are several resonances derived from the antibonding π^* and $3\sigma^*$ orbitals with different symmetries and energies that could be involved in different ways in the inelastic tunneling and could be explored by changing the polarity of the bias and the lateral position of the tip with respect to the adsorbed molecule.[30]

V. CONCLUDING REMARKS

We have examined atom transfer or, more generally, potential barrier crossing resulting from coherent multiple excitation of a bond by inelastic tunneling of a single electron (or hole) via a negative- (or positive-) ion resonance. This mechanism is analogous to the process of desorption induced by electronic transitions, but with electrons (or holes) provided by tunneling between a tip and a substrate. An important difference is the possibility to control, through the applied voltage, the occupancy of the resonance by the tunneling electrons and also the possibility to probe a positive-ion resonance by changing the polarity of the bias.

Earlier theories of atom transfer using the tip of a scanning tunneling microscope have been based on a DIMET-like mechanism, where atom transfer results from incoherent multiple excitations produced by sequential inelastic scattering of tunneling electrons. This latter mechanism gives rise to a quasi-Boltzmann distribution of vibrational states corresponding to a vibrational heating, while the coherent multiple excitations are not distributed in a Boltzmann-like manner. At low biases, we find that the rate of coherent multiple excitation is also nonlinear, in particular for excitations to high-lying vibrational levels resulting in atom transfer, in a manner not unlike the incoherent excitation rates. However, the transfer rate is found to depend critically on the polarity in a manner which depends on whether the resonance is nearly full or empty, whereas the rate resulting from incoherent multiple excitations (vibrational heating) is relatively independent of the polarity.

The coherent multiple excitation mechanism is shown to be most important at low currents, where the average time between electron tunneling events is longer than the vibrational lifetime, while the incoherent multiple excitations dominate at higher currents. For instance, the relatively long vibrational lifetime for Xe on Ni means the observed transfer rate is dominated by incoherent multiple excitations. However, there are many other adsorption systems, illustrated here by Na on Cu and O_2 on Pt, where the vibrational lifetime is much shorter, and as a result coherent multiple excitation could play a significant role in atom transfer or bond breaking. Finally, we note that in this work, our single-particle theory has been limited to nearly full or nearly empty adsorbate-induced resonances and to a truncated oscillator model for the barrier crossing problem. In principle it should be possible to deal with a more realistic potential barrier in the impulsive collision limit by using the theory developed in electron-molecule scattering,[31] while the many-electron problem of dealing with a partially occupied resonance requires further developments of the theory.

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APPENDIX

The result in Eq. (5) can be obtained in a manner which is easily generalized to transitions out of levels other than the ground state ($n = 0$). For $m\hbar\omega \ll \Gamma$ the denominator of Eq. (1) can be expanded as

$$\frac{1}{(\epsilon_r-\epsilon_i)+\hbar\omega m-i\Gamma/2}=\sum_{j=0}^{\infty}\frac{(-m\hbar\omega)^j}{[(\epsilon_i-\epsilon_r)+i\Gamma/2]^{j+1}}\,. \tag{A1}$$

Using $\sum_{m=0}^{\infty}\langle n|m\rangle m^j\langle m|k\rangle = \langle n|\widehat{m}^j|k\rangle$ then yields

$$P_{k\to n}(\epsilon_i)\simeq\frac{\Gamma}{2\pi}\left|\sum_{j=0}^{\infty}\frac{(-\hbar\omega)^j\langle n|\widehat{m}^j|k\rangle}{[(\epsilon_i-\epsilon_r)+i\Gamma/2]^{j+1}}\right|^2 . \tag{A2}$$

Since $\widehat{m}$ corresponds to the number operator for the displaced harmonic oscillator, it can be written in terms of creation and annihilation operators for $V_0(z)$: $\widehat{m} = \widehat{b}^\dagger\widehat{b} + \lambda(\widehat{b}^\dagger + \widehat{b})$, where λ is a coupling constant which relates to the force on the adsorbate in $V^*(z)$: $\lambda = F/(2m\hbar\omega^3)^{1/2}$. The lowest-order nonzero term will be that with $j = |n-k|$. If higher-order terms can be ignored [in the limit $(n\lambda\hbar\omega/\Gamma)^2 \ll 1$] then for $n > k$, Eq. (A2) reduces to

$$P_{k\to n}(\epsilon_i)\simeq\frac{n!\Gamma}{2\pi k!}\frac{(\lambda\hbar\omega)^{2n}}{[(\epsilon_r-\epsilon_i)^2+\Gamma^2/4]^{n+1}}. \tag{A3}$$

In the case $k = 0$, this is the same as Eq. (5).

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[1] J.A. Stroscio and D.M. Eigler, Science **254**, 1319 (1991).

[2] R.S. Becker, G.S. Higashi, Y.J. Chabal, and A.J. Becker, Phys. Rev. Lett. **65**, 1917 (1991).

[3] I.W. Lyo and P. Avouris, J. Chem. Phys. **93**, 4479 (1990).

[4] G. Dujardin, R.E. Walkup, and P. Avouris, Science **255**, 1232 (1992).

[5] I.W. Lyo and P. Avouris, Science **253**, 173 (1991).

[6] D.M. Eigler, C.P. Lutz, and W.E. Rudge, Nature **352**, 600 (1991).

[7] N.D. Lang, Phys. Rev. B **45**, 13 599 (1992).

[8] J.J. Sáenz and N. García, Phys. Rev. B **47**, 7537 (1993).

[9] S. Gao, M. Persson, and B.I. Lundqvist, Solid State Commun. **84**, 271 (1992); J. Electron. Spectrosc. Relat. Phenom. **64/65**, 665 (1993).

[10] R.E. Walkup, D.M. Newns, and P. Avouris, Phys. Rev. B **48**, 1858 (1993); J. Electron. Spectrosc. Relat. Phenom. **64/65**, 523 (1993).

[11] See, for instance, DIET V, edited by A.R. Burns, E.B. Stechel, and D.R. Jennison (Springer, Berlin, 1993).

[12] S.A. Buntin, L.J. Richter, R.R. Cavanagh, and D.S. King, Phys. Rev. Lett. **61**, 1321 (1988).

[13] R.E. Palmer and P.J. Rous, Rev. Mod. Phys. **64**, 383 (1992).

[14] J.A. Prybyla, T.F. Heinz, J.A. Misewich, M.M.T. Loy, and J.H. Glownia, Phys. Rev. Lett. **64**, 1537 (1990).

[15] J.W. Gadzuk, Phys. Rev. B **44**, 13 466 (1991).

[16] B.N.J. Persson and M. Persson, Solid State Commun. **36**, 175 (1980).

[17] B.N.J. Persson and A. Baratoff, Phys. Rev. Lett. **59**, 339 (1987).

[18] D.M. Eigler, P.S. Weiss, E.K. Schweizer, and N.D. Lang, Phys. Rev. Lett. **66**, 1189 (1991).

[19] E.W. Montroll and K.E. Shuler, Adv. Chem. Phys. **1**, 361 (1958).

[20] E.J. Heller, J. Chem. Phys. **62**, 1544 (1975).

[21] J.W. Gadzuk, Phys. Rev. B **31**, 6789 (1985).

[22] N.S. Wingreen, K.W. Jacobsen, and J.W. Wilkins, Phys. Rev. B **40**, 11 834 (1989).

[23] J. Leiro and M. Persson, Surf. Sci. **207**, 473 (1983).

[24] S.Å. Lindgren, C. Svensson, and L. Wallden, Phys. Rev. B **42**, 1467 (1990).

[25] The phonon damping rate has been determined from the vibrational line shape calculated using the same technique as in Ref. 23 with a simple nearest-neighbor force constant model.

[26] F.J. Kao, D.G. Busch, D. Cohen, D. Gomes da Costa, and W. Ho, Phys. Rev. Lett. **71**, 2094 (1993).

[27] H. Steininger, S. Lehwald, and H. Ibach, Surf. Sci. **123**, 1 (1982).

[28] L. Šiller, J.F. Wendelken, K.M. Hock, and R.E. Palmer, Chem. Phys. Lett. **210**, 15 (1993).

[29] D. Langreth, Phys. Rev. Lett. **54**, 126 (1985).

[30] B. Hellsing, Surf. Sci. **282**, 216 (1993).

[31] J.N. Bardsley and F. Mandl, Rep. Prog. Phys. **31**, 471 (1968).

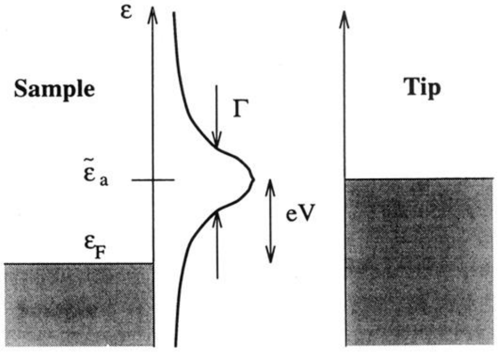

FIG. 1. Model of the electronic structure of the tip-sample system, with an atom adsorbed on the sample.