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Vibrational heating in single-molecule switches: an energy-dependent density-of-states approach

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Abstract

In recent experiments, it has been shown that the switching rate of single-molecule switches can show a rather complicated dependence on the applied bias voltage. Here, we discuss a minimal model which describes the switching process in terms of inelastic scattering processes of the tunneling electron by specific molecular vibrations. One important point is the introduction of an energy-dependent electronic density of states around the Fermi energy. The influence of different model parameters on the switching rate is studied and we show that the inclusion of a variable density of states allows us to understand the non-monotonic behavior of the switching rate observed in some experiments.

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the formulation of Moore's law [1] industry has struggled to keep up with it, but in the near future the minimum feature size in integrated circuits will reach the size of a few atoms and quantum tunneling, e.g. through the gate of a transistor, is already an unavoidable problem. A promising strategy to overcome such limitations of semiconductor-based technologies is molecular electronics, where electronic functionalities are implemented at the molecular scale [2]. Although the first proposal of a molecular scale device was made in 1974 by Aviram and Ratner [3] it was not till the mid-1990s that significant breakthroughs were achieved [4–7]. Different molecular scale functionalities (diodes, transistors, switches, etc) have meanwhile been demonstrated and studied both theoretically and experimentally, see [2, 8] for comprehensive reviews. The emerging picture is that such functional behavior results from a very delicate interplay between chemical composition, molecular topology, vibrational dynamics and electronic structure. For instance, the realization of single-molecule switches imposes very strong conditions on the structural and electronic properties of potential molecular candidates.

In order to realize a reversible molecular switch the system must have several (at least two) stable states. Furthermore, it must be possible to change between the different forms of the molecular system reversibly by the application of an external stimulus. Bi-stability in molecular junctions is a widely observed phenomenon. To the best of our knowledge, the first 'molecular switch' was reported by Eigler *et al* [4]. In their groundbreaking experiment they succeeded in reversibly switching a xenon atom between being on an Ni(110) surface and being attached to the tip of a scanning tunneling microscope (STM). This experiment also inspired several theoretical investigations which tried to explain the observed exponential dependence of the switching rate on the applied bias voltage [9–13]. Moreover, experimental groups have created other molecular or atomic switches [7, 14]. The direct observation of the quantum tunneling of single hydrogen atoms with an STM by Lauhon and Ho [15] was not only another example for a possible realization of a switch of atomic size, but also a big step towards the complete understanding of the dynamical behavior of a molecular switch. More recently, reversible switching in molecular systems has been achieved alternatively by inducing conformational changes either by the scattering of

the tunneling electrons [16] or by light [17]. In particular, the group of azobenzene molecules has attracted much attention [16–23]. In 2007 Liljeroth *et al* measured the spatial and energy dependence of the rate for the current-induced hydrogen tautomerization in a single naphthalocyanine molecule [24]. This demonstrates the importance of the energetic position of the molecular orbital with respect to the chemical potential of the leads, as well as the spatial structure of the molecular orbital through which the current is passing.

In this paper, we will study the basic properties of a minimal model to describe switching induced by the coupling of a tunneling charge to molecular vibrational degrees of freedom. The model was originally proposed by Gao *et al* [13] and it was extended by us [25] to include the influence of an energy-dependent electronic density of states around the Fermi level. However, the influence of different model parameters on the behavior of the switching rates remained elusive and it will be addressed in some detail here.

This paper is organized as follows. In section 2, we present a short overview over different single-molecule switches and possible classification schemes. The vibrational heating model and the influence of the different model parameters on the switching rate are discussed in section 3. We end with concluding remarks in section 4.

2. Bi-stability in single-molecule switches

In general, molecular switches can be divided into different classes depending on different aspects of the system or on the underlying switching mechanism. One classification scheme is based on a division of molecular switches into intrinsic and extrinsic switches. In the first case the molecular system itself undergoes a transformation into a new charged or conformational state, while in the second case the switching can be related to an extrinsic property, e.g. a change in the lead–molecule coupling if a molecule adsorbs differently depending on the applied bias voltage [26]. The experiment on an Xe atom on an Ni(110) surface done by Eigler *et al* [4] is clearly an example of extrinsic switching, while the hydrogen tautomerization reaction in a single naphthalocyanine molecule [24] represents an intrinsic molecular switch. The class of intrinsic switches can further be divided into two different ‘sub-classes’: conformational switches and redox switches [8]. In both cases, intrinsic molecular properties are changed; in the former case the conformation of the molecule, e.g. the position of an atom or a molecular sidegroup, and in the latter case the charge-state.

Another classification scheme distinguishes between the physical mechanisms underlying the switching phenomenon [8, 19]. Several physical mechanisms have been proposed to explain the observed dependence of the switching rate on the different extrinsic properties of the systems under investigation. The first class is the redox-potential-induced switching, i.e. charging the system [27–29] or chemically modifying it [30]. The second class of physical mechanisms is field-induced switching [18, 31–33], e.g. using the electric field between the tip of an STM and the substrate, or a magnetic field to switch between the different stable states. In

many experiments with the class of azobenzene molecules, the conformational change is induced by UV light. Thus, a third class is the light-induced switching [17, 19, 22, 23, 34, 35]. Furthermore, one can also ‘force’ the molecule into different conformations mechanically [36–39] or thermally activate the switching process [40, 41]. The last, and perhaps most important, class of physical mechanisms is current-induced switching in which the switching is triggered by the inelastic scattering of the tunneling electrons in the molecular/atomic system [4, 13, 15, 21, 25, 42–61]. In the case where the electrons are inelastically scattered by vibrations of the molecule and at least n such vibrations, each of energy $\hbar\omega$, are needed to induce the switching, Gao *et al* showed that the switching rate shows a power-law dependence on the applied bias voltage $R \propto V_{\text{bias}}^n$ [13]. This mechanism is usually called vibrational heating. Deviations of the measured switching rate from the power-law dependence [12, 25, 44, 61] can be explained either by combining the vibrational heating with other switching mechanisms (e.g. quantum tunneling [54]) or by the breakdown of the approximations used in [13]. In 2004, Tikhodeev and Ueba extended the model of Gao *et al* to include effects of an effective bath temperature (i.e. the phonon distribution function in the leads is not the equilibrium one) and adsorbate vibrational lifetime broadenings (i.e. the vibrational density of states (DOS) of the molecule is broadened due to the interaction with the substrate) [43]. These changes lead to a deviation from a simple power-law dependence of the switching rate on the bias voltage in the vicinity of and below the threshold voltage, $V_{\text{bias}} = \hbar\omega$. However, in [43] the adsorbate electronic DOS is still assumed to be constant over the relevant energy range. In many experiments on atomic switches this assumption is valid since the electrons tunnel primarily through a resonance which is situated far from the Fermi energy of the leads, but one important characteristic of molecular switches is the non-constant electronic DOS near the Fermi energy. This can change the dependence of the switching rate on the bias voltage dramatically as shown in [25].

3. Vibrational heating in single-molecule switches

In the so-called vibrational heating mechanism for atom transfer proposed independently by Gao *et al* [9, 13] and Walkup *et al* [12], the adsorbate gathers energy to overcome the potential barrier by inelastic scattering of the tunneling electron with vibrations of the molecule. At the same time the molecule loses energy to electron–hole pairs and other processes, e.g. phonon–vibron coupling between the leads and the molecule. In [25] we applied such ideas to describe the switching of the carboxylic oxygen in a PTCDA STM junction. Here we discuss the influence of the different model parameters on the bias dependence of the switching rate and the differences of our theory to the original vibrational heating model of Gao *et al* [13].

In the following we want to sketch the derivation of the excitation and relaxation rates of molecular vibrations due to inelastic scattering with tunneling electron and electron–hole pair creation in a typical molecular junction, in which the

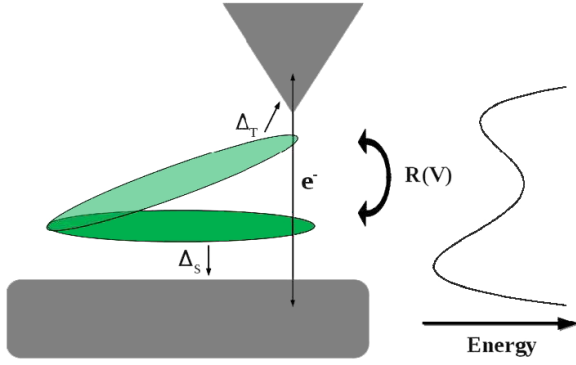


Figure 1. Schematic representation of a single-molecule switch in an STM junction in which the molecule is asymmetrically coupled to the surface and the STM tip ($\Delta_s > \Delta_t$). The molecule gathers energy to overcome the potential barrier between the two stable positions by inelastic scattering of the tunneling electron.

molecule is contacted by at least two leads α (e.g. left and right leads in a break-junction set-up or STM tip and surface in an STM-based single-molecule switch; cf figure 1). The Hamiltonian of the combined molecule–lead system has the following form:

$$H = \sum_{\alpha,k} \varepsilon_{\alpha,k} c_{\alpha,k}^\dagger c_{\alpha,k} + \varepsilon_m c_m^\dagger c_m + \hbar\omega b^\dagger b + \sum_{\alpha,k} (T_{\alpha,km} c_{\alpha,k}^\dagger c_m + \text{H.c.}). \quad (1)$$

The operator $c_{\alpha,k}^\dagger$ and c_m^\dagger creates an electron in the state $|k\rangle$ and $|m\rangle$ of the lead α and the molecule, respectively, with the corresponding energies $\varepsilon_{\alpha,k}$ and ε_m . The hopping between the leads and the molecular level is described by the last term in equation (1). The number of vibrations $\hbar\omega$ of the molecule is given by $b^\dagger b$. In the following we assume that ε_m is a linear function of the vibrational coordinate q , $\varepsilon_m(q)$; ω is the frequency of the molecular vibration with the normal coordinate $q = \sqrt{\hbar/(2M\omega)}(b^\dagger + b)$ and mass M . The electron–vibron coupling can then be modeled by

$$H_{e-v} = \lambda_0(b^\dagger + b)(c_m^\dagger c_m), \quad (2)$$

where $\lambda_0 = \sqrt{\hbar/(2M\omega)}\varepsilon'_m$, with $\varepsilon'_m = \partial\varepsilon_m/\partial q$ at $q = 0$. Since the interaction between the vibrational system and the adsorbate electronic states is, in general, weak, it can be treated by first-order perturbation theory. Thus, only the excitation and relaxation rates, Γ_\uparrow and Γ_\downarrow , between the vibrational ground state and the first excited state are required. These rates can be calculated using first-order perturbation theory, i.e. Fermi's golden rule:

$$\Gamma_\uparrow = 2\frac{2\pi}{\hbar} \sum_{j,l} | \langle j, 1 | H_{e-v} | l, 0 \rangle |^2 f_l (1 - f_j) \delta(\varepsilon_j - \varepsilon_l + \hbar\omega), \quad (3)$$

$$\Gamma_\downarrow = 2\frac{2\pi}{\hbar} \sum_{j,l} | \langle j, 0 | H_{e-v} | l, 1 \rangle |^2 f_l (1 - f_j) \delta(\varepsilon_j - \varepsilon_l - \hbar\omega) \quad (4)$$

with 0 and 1 denoting the vibrational ground state and the first excited state, respectively, while j and l denote any of the stationary one-electron states of the leads (with corresponding Fermi–Dirac distributions $f_{j,l} = 1/\{1 + \exp[(\varepsilon - \mu_{j,l})/(k_B T)]\}$, and H_{e-v} denotes the electron–vibration interaction in equation (2).

These rates describe the vibrational excitation and relaxation induced by the tunneling electrons and can be decomposed into $\Gamma_{\uparrow,\downarrow}^{\alpha\alpha}$ and $\Gamma_{\uparrow,\downarrow}^{\alpha\beta}$ depending on whether the final and initial state (first and second superscript) of the tunneling electron is in the same lead or not. We model the adsorbate electronic DOS by a Lorentzian shape, $\rho_m^\alpha(E) = \Delta_\alpha/(\pi((E - \varepsilon_m)^2 + \Delta^2))$, where $\Delta = \sum_\alpha \Delta_\alpha$, with Δ_α describing the electronic coupling between the molecular level and lead α . In the low temperature limit the excitation and relaxation rates can be calculated analytically. The term $\Gamma_{\downarrow}^{\alpha\alpha}$ is given by

$$f_\pm(E) = \frac{4\lambda_0^2}{\pi \Delta \hbar^2 \omega (4\Delta^2 + \hbar^2 \omega^2)} \left(\hbar\omega \tan^{-1} \left[\frac{E - \varepsilon_m}{\Delta} \right] \pm \Delta \log[\Delta^2 + (E - \varepsilon_m)^2] \right), \quad (5a)$$

$$\Gamma_{\downarrow}^{\alpha\alpha} = \Delta_\alpha^2 (f_+(\mu_\alpha + \hbar\omega) - f_+(\mu_\alpha) + f_-(\mu_\alpha) - f_-(\mu_\alpha - \hbar\omega)), \quad (5b)$$

where μ_α is the chemical potential of lead α . The excitation rates $\Gamma_{\uparrow}^{\alpha\alpha}$ become zero in the low temperature limit, because of the Pauli exclusion principle. The Pauli exclusion principle also reduces the number of transition rates $\Gamma_{\uparrow,\downarrow}^{\alpha\beta}$ one has to calculate, because the electrons can only tunnel from the lead with the higher chemical potential to the one with the lower chemical potential. The transition rates $\Gamma_{\uparrow,\downarrow}^{\alpha\beta}$ can be written as

$$\Gamma_{\downarrow}^{\alpha\beta} = \Delta_\alpha \Delta_\beta (f_+(\mu_\beta + \hbar\omega) - f_+(\mu_\alpha) + f_-(\mu_\beta) - f_-(\mu_\alpha - \hbar\omega)), \quad (6a)$$

$$\Gamma_{\uparrow}^{\alpha\beta} = \Delta_\alpha \Delta_\beta (f_+(\mu_\beta) - f_+(\mu_\alpha + \hbar\omega) + f_-(\mu_\beta - \hbar\omega) - f_-(\mu_\alpha)) \quad \forall |\mu_\beta - \mu_\alpha| \geq \hbar\omega, \quad (6b)$$

where lead α is the one with the lower chemical potential (i.e. $\mu_\alpha = -|V_{\text{bias}}/2|$ for symmetrically applied bias like in a break-junction experiment and assuming $\varepsilon_{F_\alpha} = 0$; $\mu_\alpha = -|V_{\text{bias}}|$ for asymmetrically applied bias like in an STM experiment). Notice that the previous equations (6) are only valid for applied bias larger than the vibrational frequency $\hbar\omega$. The inelastic transition rates between the vibrational ground state and first excited state, specified in equations (5) and (6), reduce to the result of Gao *et al* in the limit of a very broad molecular state. This can be shown by expanding the \tan^{-1} and the log in equation (5a) in a power series up to second order and assuming $\Delta \gg \hbar\omega$ and $|V_{\text{bias}}| \gg \hbar\omega$.

The transfer between the two wells of a double well, as depicted in figure 1, in general involves various processes as already outlined above. Here we want to use the simplest possible model to calculate the transfer rate. Thus, we concentrate on the vibrational heating process and use a truncated harmonic oscillator, as introduced in [13], to

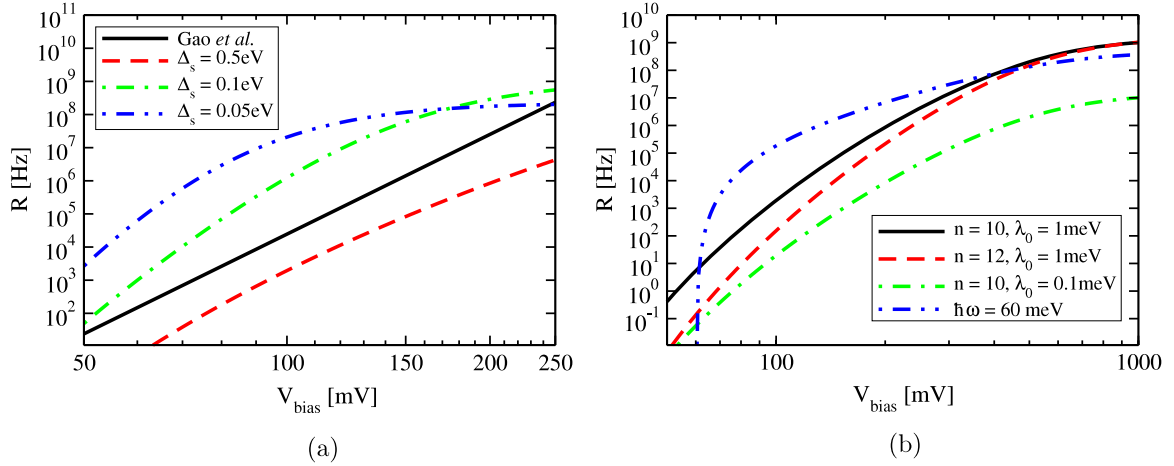


Figure 2. (a) Calculated transfer rate R for different substrate–molecule coupling Δ_s (other parameters: $\Delta_t = 0.1\Delta_s$, $\hbar\omega = 20$ meV, $n = 10$, $\lambda_0 = 1$ meV, $\varepsilon_m = 0$ eV) and calculated transfer rate of the model of Gao *et al* (parameters: $\Delta_t = 0.1\Delta_s$, $\Delta_s = 0.5$ eV, $\hbar\omega = 20$ meV, $n = 10$, $\gamma = 1.5 \times 10^8$ s $^{-1}$, $\gamma_{ch} = 10^8$ s $^{-1}$). (b) Calculated transfer rate R for different numbers n of levels in the potential well as well as for different electron–vibron couplings λ_0 (other parameters: $\Delta_s = 0.5$ eV, $\Delta_t = 0.1\Delta_s$, $\hbar\omega = 20$ meV, $\varepsilon_m = 0$ eV) and calculated rate for different vibrational energy (parameters: $\Delta_s = 0.5$ eV, $\Delta_t = 0.1\Delta_s$, $\lambda_0 = 1$ meV, $\varepsilon_m = 0$ eV, $n = 3$).

describe the barrier crossing. The transfer rate R can be expressed as a product of the transition into level n and an effective Boltzmann factor (with characteristic temperature $T_v = \hbar\omega / (k_B \ln[\Gamma_{\downarrow} / \Gamma_{\uparrow}])$) describing the probability to arrive at the sub-critical level $n - 1$ where the transition takes place [13]:

$$R \simeq n\Gamma_{\uparrow} \exp\left[\frac{(n-1)\hbar\omega}{k_B T_v}\right] = n\Gamma_{\uparrow} \left(\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}}\right)^{n-1}. \quad (7)$$

In the limit of a constant DOS around the Fermi energy the transfer rate is proportional to the applied bias voltage, $R \propto V_{\text{bias}}^n$, as shown by Gao *et al*. However, in general the above expression does not yield a simple power-law dependence on the applied bias, as shown below.

In the following, we will concentrate without loss of generality on single-molecule switches in a typical STM set-up, see figure 1. Thus, we will assume that the molecule is asymmetrically coupled to the leads, with one contact being the surface (sub-/superscript s) and the other contact being the STM tip (sub-/superscript t). The bias voltage is applied to the surface. Figure 2(a) shows the dependence of the transfer rate, equation (7), on different substrate–molecule coupling Δ_s . In the case of a sharp resonance, $\Delta_s = 0.05$ eV, the transfer rate first increases exponentially and then saturates. With increasing coupling the electronic DOS near the Fermi energy becomes flat, and thus also the dependence of the rate on V_{bias} converges to the power-law behavior as described by Gao *et al* [13], which is also shown in figure 2(a) as a solid black curve. Using a non-constant electronic DOS near the Fermi energy thus changes the linear dependence of the transfer rate on the bias voltage in a log–log plot to a more complex behavior. In general, the slope and the curvature of the rate now depend not only on the number of vibrations n or on the coupling Δ but also on the vibrational energy $\hbar\omega$, as can be seen in figure 2(b). For large applied bias voltage the rate becomes constant, which is in stark contrast to the

original vibrational heating model by Gao *et al* [13]. The limit of the transfer rate in our extended model can be calculated analytically and it depends strongly on the electronic coupling of the molecular level to the leads Δ and also on the barrier height $n\hbar\omega$. Furthermore, in the case of asymmetric coupling like in an STM junction, the limit also depends on the position of the molecular level relative to the Fermi energy of the lead to which it is coupled more strongly. Figure 2(b) also shows that the transfer rate is proportional to λ_0^2 .

However, in a typical STM-based molecular junction the molecular level is not fixed at a certain position as assumed in Figure 2, but it is strongly coupled to the chemical potential of the metallic surface. In situations where the DOS in the bias window changes strongly (i.e. sharp peaks entering the bias window) the transfer rate can deviate strongly from the power-law dependence on the applied bias voltage as shown in figure 3. If the molecular level gets into resonance with the Fermi energy of the STM tip and if the electronic coupling to the surface is not too strong (Δ_s small) the transfer rate can show a constant behavior for a certain bias range or even decrease (cf figure 3(a)). The origin of this behavior can be identified by having a closer look at the different transition rates, $\Gamma_{\downarrow}^{ss,tt}$ and $\Gamma_{\uparrow,\downarrow}^{st}$. While the transition rate Γ_{\downarrow}^{ss} is constant because the position of the molecular level relative to the chemical potential of the surface is constant, the rates $\Gamma_{\uparrow,\downarrow}^{st}$ increase until the molecular level is completely within the bias window. Both transition rates, Γ_{\uparrow}^{st} and Γ_{\downarrow}^{st} , are shifted relative to each other and this shift is related to the vibrational energy $\hbar\omega$, cf equation (6). The rate Γ_{\downarrow}^{tt} at which the molecular vibrational energy dissipates into the tip has a maximum when the molecular level is in resonance with the Fermi energy of the tip, as shown in figure 3(b). These different behaviors lead to the strong deviation from the power-law dependence on the applied bias voltage as shown in figure 3(a). Since the DOS near the Fermi energy is assumed to be constant in the model of Gao *et al* [13] the model also fails in describing such a change in the transfer rate.

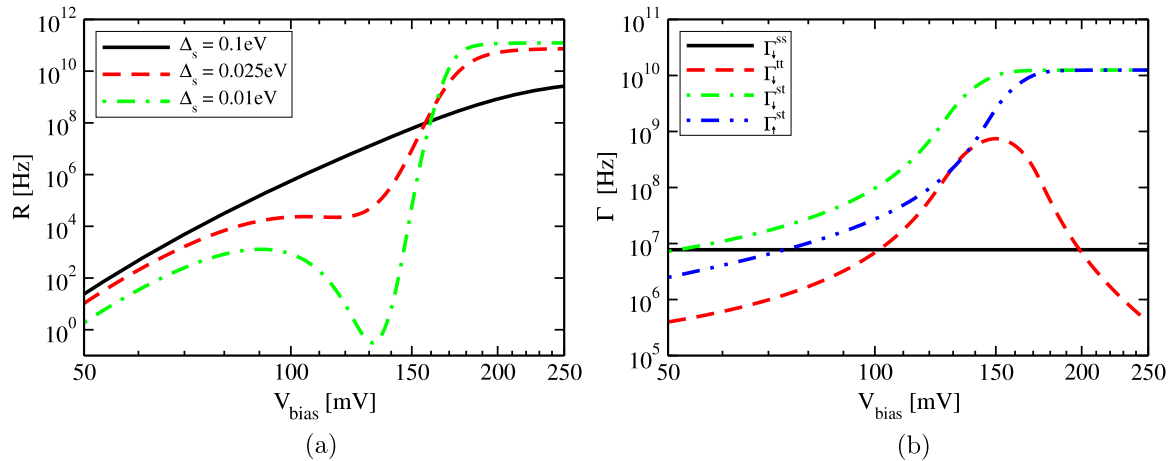


Figure 3. (a) Calculated transfer rate R for the position of the molecular level, ε_m , being coupled to the chemical potential of the substrate and different molecule–substrate coupling, Δ_s . (b) Calculated transition rates Γ for the dashed–dotted green curve in (a) (other parameters: $\varepsilon_m = 0.15\text{ eV} - V_{\text{bias}}$, $\Delta_t = 0.1\Delta_s$, $\hbar\omega = 20\text{ meV}$, $n = 10$, $\lambda_0 = 1\text{ meV}$).

Furthermore, in an STM-based single-molecule switch, the transfer rate of the molecule between two stable positions can show a strong dependence on the bias polarity. If the electrons tunnel, for example, through the lowest unoccupied molecular orbital the transfer rate for positive applied bias voltage is always larger than that for negative bias, since the position of the molecular level, and hence also the transfer rate, depends on the applied bias (the molecular level moves with the chemical potential of the surface, i.e. $\varepsilon_m(V_{\text{bias}}) = \varepsilon_m^0 \pm |V_{\text{bias}}|$).

This variation of the transfer rate with the position of the molecular level also suggests another possible feature of single-molecule switches. In a break-junction experiment one could use a gate voltage to shift the position of the molecular level in and out of the bias window. In this way the switching frequency could be easily tuned between 10 kHz and 1 GHz.

4. Conclusions

In recent experiments it has been shown that the switching rate can deviate strongly from the simple power-law dependence on the applied bias as proposed by Gao *et al* [25, 61]. This different behavior, which cannot be described by, for example, field-induced switching, suggested that the original vibrational heating model needs to be improved to include an energy-dependent electronic DOS near the Fermi energy. We have considered an energy-dependent DOS and discussed in detail the influence of different model parameters on the switching rate. For some limiting cases where the DOS near ε_F is nearly constant the extended model shows the same behavior like the original vibrational heating model. However, we also showed that the rate saturates with increasing applied bias voltage. Furthermore, if a molecular level is coupled less strongly to the surface, i.e. the broadening is small, the switching rate of the molecule can even decrease. This is due to an increased vibrational energy dissipation into one of the leads similar to the cooling mechanisms proposed by Galperin *et al* [62]. Our results show that a complex and rich behavior

of the switching rate can be obtained by including an energy dependence of the molecular DOS around the Fermi energy. We hope that the current investigation will trigger further experimental studies on the dependence of switching rates on specific molecular properties.

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