

Vibronic effects in off-resonant molecular wire conduction

Alessandro Troisi^{a)} and Mark A. Ratner

Department of Chemistry, Materials Research Center and Center for Nanofabrication and Molecular Self-Assembly, Northwestern University, Evanston, Illinois 60208

Abraham Nitzan

School of Chemistry, The Sackler Faculty of Science, Tel Aviv University, Tel Aviv, 69978, Israel

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A model for the calculation of the inelastic contribution to the low-bias electron transport in molecular junctions is presented. It is an extension to the inelastic case of the Green's function approach to the calculation of the conduction of such systems. The model is suited for the calculation in the off-resonance regime (where molecular levels are far from the Fermi energy) and in the low bias limit, a typical situation encountered in inelastic electron tunneling measurements. The presentation of a general model is followed by the introduction of several approximations that make the calculation feasible for many systems of interest. *Ab initio* calculations of the vibronic coupling that leads to inelastic contribution to the conductance are performed for several molecules (butadiene, biphenyl, dipyrrole, and dithiophene), representative of possible molecular wires. The role of inelastic conduction is then quantified without empirical parameters and the vibrational modes that dominate the process are identified. The situations where the inelastic mechanism is particularly relevant are considered. The limits of this approach for the resonant case are also discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1556854]

I. INTRODUCTION

Increasing experimental effort is currently aimed at elucidating the conduction properties of metal–molecule–metal junctions, such as molecular wires (MW) connecting metal leads.^{1–13} This effort is largely motivated by the expectation that such systems will form the basis for molecular level electronics.^{14,15} Theoretical understanding of such processes has greatly improved^{16,17} since the seminal theories developed for the interpretation of the scanning tunneling microscope (STM) images.^{18,19} Following earlier studies of simple models,^{20,21} quantum chemical descriptions of MW have employed semiempirical,^{22–26} *ab initio*,²⁷ and density functional theory (DFT)^{28–31} Hamiltonians to make quantitative level calculations. These and other approaches^{32–35} focus on the elastic mechanism of electron transport in which the energies of the incoming and transmitted electrons are equal, and they mostly use the Landauer formula³⁵ as a starting point for a scattering theory approach to conduction.³⁶

The interaction between nuclear and electronic motions in molecular wires can manifest itself in several ways. First, it influences the absolute current, i.e., the conduction of the wire. In the strong thermal coupling limit this leads to a fully incoherent mechanism, often referred to as sequential transport or hopping. This happens when states localized on the wire become thermally populated, implying a strong temperature effect. Hopping transport in this limit is usually described in the framework of an appropriate master equation.^{37–40} Intermediate situations, in which conduction is only partly incoherent, also exist and may be analyzed by various theoretical methods^{41–43} such as a steady state analy-

sis of the Redfield equation⁴⁴ or application of the nonequilibrium Green's function formalism.³⁶ Identification^{45,46} and modeling⁴⁰ of the hopping mechanism in biological donor-bridge-acceptor systems allowed the understanding of very long-range electron transfer in such systems. Short MW operating in the off-resonance regime do not show this mechanism, because their conducting electronic states are not thermally accessible.

Second, when energetic constraints are satisfied, the electron crossing the junction may exchange a definite amount of energy with the molecular nuclear degrees of freedom, resulting in an inelastic component in the transmission current. Inelastic tunneling across thin films was first observed in 1966⁴⁷ and it is the basis for the well-established inelastic electron tunneling spectroscopy (IETS) technique used in the characterization of metal surfaces covered by adsorbates.^{48,49} Ho and co-workers^{7,50–52} have observed IETS for single molecules adsorbed on a metal surface, using a STM apparatus (IETS-STM). This observation is important both because it gives structural information on the molecular junction and because it provides a direct access to the dynamics of energy relaxation and consequently thermal dissipation during the tunneling. In the context of molecular wire conduction this issue has significant technological implications. A reformulation of such theory may take advantage of the current understanding of molecular level conduction and the improved capability of quantum chemistry to model molecular junctions.

Recent theoretical efforts^{53–62} on the inelastic transport in MW have mainly focused on the phenomenology of inelastic tunneling studied through the definition of suitable model Hamiltonians and the numerical evaluation of the transmission function. The adopted form for the vibronic

^{a)}Electronic mail: atroisi@chem.nwu.edu

coupling term in the effective Hamiltonians includes the Holstein-type coupling,^{53–55} and the SSH-like coupling⁵⁶ in its semiclassical⁵⁷ and quantum⁵⁸ version. The vibronic coupling itself appears as a parameter in these models. More quantitative analyses have been presented by Mingo and Makoshi,⁶⁰ who employed an extended Huckel Hamiltonian and a scattering formalism, and by Lorente *et al.*,⁶¹ who based their study on the Tersoff–Hamman theory of tunneling.¹⁸ It is important to distinguish between the off-resonance inelastic tunneling, considered here and pertinent to the IETS measurement, and the inelastic effects related to the polaron formation on the MW, two different problems often studied with closely resembling model Hamiltonians.

We present a model for the inelastic electron tunneling to be used in conjunction with *ab initio* evaluation of the relevant vibronic couplings. The aim is to develop a parameter free calculation of inelastic conduction, quantifying its role with respect to the elastic channel. The formalism, developed in Sec. II, generalizes the approach of Ref. 20, which showed good results in its *ab initio* implementation.²⁶ It allows the calculation of the inelastic contribution to molecular conductance without any external parameter for virtually any molecule and vibrational mode. Reliable vibrational normal modes may be calculated at the same level of the electronic and vibronic coupling, making the description entirely consistent. In Sec. III, we set the computational model to calculate the relevant vibronic coupling for several realistic wires, adopting a simplified description of the molecule–metal contact. The vibrational modes that dominate the inelastic transport are identified, and propensity rules are drawn for the considered organic compounds. Some circumstances leading to enhanced inelastic tunneling are also discussed. Section IV presents some conclusions.

II. THE MODEL

A. Background

Working in the adiabatic Born–Oppenheimer approximation, the purely electronic Hamiltonian of the junction may be considered parametrically dependent on the nuclear coordinates $\{Q_\alpha\}$. We will first consider a single nuclear degree of freedom of the molecule and generalize to n modes later. The one-electron Hamiltonian is partitioned as usual as¹⁷

$$H(Q) = H_L + H_R + H_M(Q) + V, \quad (1)$$

where the suffixes L , R , M stand for left and right electrode, and the molecule, respectively, and V is the interaction between the subsystems [Fig. 1(a)].

The “molecule” considered here is an “extended molecule,” i.e., a subsystem large enough so that the properties of the remaining electrode subsystems are close to those of pure metals. In this context the M subsystem extends until all the vibrational modes relevant to the inelastic tunneling are localized on its inside, and the coupling V does not depend on Q . We are assuming that the modes of the system can be separated in “molecular vibrations,” localized on the junction, and phonons, delocalized on the metallic leads. The latter do not affect the molecular transport properties and are ignored in the Hamiltonian of Eq. (1). In this extended mol-

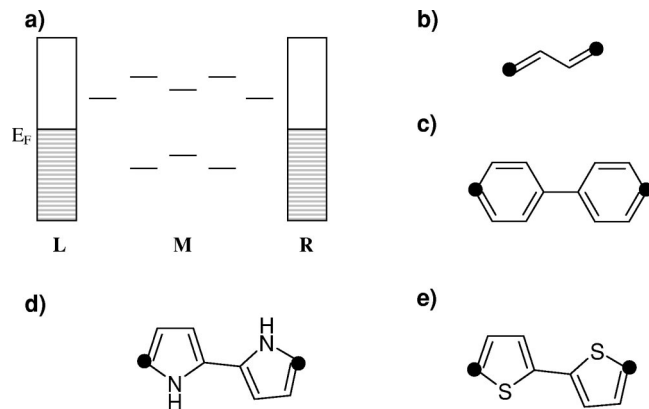


FIG. 1. (a) Schematic representation of the one-electron energy levels localized on the left (L) and right (R) leads and on the molecule (M). In the computations presented in Sec. III it is assumed that only two orbitals per molecule interact, respectively, with the right and left electrode. For the molecule considered in this work, (b) butadiene, (c) biphenyl, (d) dipyrrole, (e) dithiophene, a black circle indicated the contact atoms. The p_z orbitals on these atoms interact with the metal.

ecule picture, the coupling V is not influenced by the localized vibrations, i.e., it does not depend on Q . The coupling between localized and delocalized modes is usually weak, as proved by vibrational spectroscopy on molecular monolayers,⁴⁹ and it is neglected here.

Following Mujica *et al.*²⁰ the conductance for this system at a given configuration is

$$g(E) = 4\pi^2 g_c \sum_{lr} |T_{lr}|^2 \delta(E_l - E) \delta(E_r - E), \quad (2)$$

where $g_c = 2e^2/h$ is the quantum conductance; the sum extends over all the states $\{l\}$ and $\{r\}$, eigenfunctions of H_L and H_R , and localized on the left and right electrodes; T_{lr} is a matrix element of the transmission operator⁶³

$$T = V + VGV, \quad (3)$$

and G is the retarded Green's function of the total Hamiltonian:

$$G(E) = (E - H + i\varepsilon)_{\varepsilon \rightarrow 0}^{-1}. \quad (4)$$

Writing the matrix element T_{lr} explicitly as

$$T_{lr} = \sum_{ij} V_{li} G_{ij} V_{jr}, \quad (5)$$

and substituting in Eq. (2) the following expression is found:²⁹

$$g(E) = g_c \text{Tr}(\Gamma^L(E) \mathbf{G}(E) \Gamma^R(E) \mathbf{G}(E)^+), \quad (6)$$

where the Γ^L and Γ^R matrices are given by

$$\Gamma_{ij}^L(E) = -2\pi \sum_l V_{li} V_{lj}^* \delta(E_l - E), \quad (7a)$$

$$\Gamma_{ij}^R(E) = -2\pi \sum_r V_{ri} V_{rj}^* \delta(E_r - E). \quad (7b)$$

These matrices are twice the imaginary part of the self-energy matrices associated with the interaction of the molecular subsystem with the metal continua. In this paper we will not deal with their explicit evaluation.

The current is given by

$$I = \int_{-\infty}^{+\infty} \frac{g(E)}{e} [f_L(E) - f_R(E)] dE, \quad (8)$$

where f_L , f_R are the Fermi functions of the left and right electrodes, assumed to be in thermal equilibrium. The external potential Φ applied on the electrodes is implicit in Eq. (8), where it enters by shifting the Fermi function as $f_\Phi = f(E - e\Phi)$. We limit our attention to the small voltage limit, in which the effect of the electric field on the molecular levels⁶⁴ may be disregarded.

It is useful to consider the simple case of a wire described by N interacting states such that only states $|1\rangle$ and $|N\rangle$ interact, respectively, with the $\{l\}$ and $\{r\}$ manifolds. This gives

$$g(E) = g_c |G_{1N}(E)|^2 \Gamma^L(E) \Gamma^R(E), \quad (9)$$

$$\Gamma^L(E) = -2\pi \sum_l |V_{l1}|^2 \delta(E_l - E), \quad (10a)$$

$$\Gamma^R(E) = -2\pi \sum_r |V_{rN}|^2 \delta(E_r - E). \quad (10b)$$

This simplified set of equations will be used in Sec. III.

B. Extension to the vibronic case

To extend the previous treatment to inelastic conduction we can define initial and final states as Born–Oppenheimer products of an electronic wave function $\psi(q, Q)$ and nuclear wave function $\Lambda(Q)$, where q and Q denote electronic and nuclear coordinates, respectively. Denoting by v and w the initial and final vibrational quantum numbers, the initial and final states (for left to right transfer) may be written as

$$\Psi_{lv}(q, Q) = \psi_l(q, Q) \Lambda_{lv}(Q), \quad (11a)$$

$$\Psi_{rw}(q, Q) = \psi_r(q, Q) \Lambda_{rw}(Q). \quad (11b)$$

The conductance, Eq. (2), may be written as a sum of contributions from all initial and final vibrational channels weighted by a Boltzmann factor P_v . We also define the contributions of electrons incident from the left and the right using, respectively, the suffixes $L \rightarrow R$ and $R \rightarrow L$:

$$g^{L \rightarrow R} = \sum_{vw} P_v(\theta) g_{vw}^{L \rightarrow R}(E), \quad (12a)$$

$$g^{R \rightarrow L} = \sum_{vw} P_v(\theta) g_{vw}^{R \rightarrow L}(E), \quad (12b)$$

$$P_v(\theta) = \exp(-\varepsilon_v/k_B\theta) / \sum_u \exp(-\varepsilon_u/k_B\theta), \quad (13)$$

where θ is the temperature and where

$$g_{vw}^{L \rightarrow R}(E) = 4\pi^2 g_c \sum_{lr} |T_{lv, rw}|^2 \delta(E_l + \varepsilon_v - E) \delta(E_r + \varepsilon_w - E), \quad (14a)$$

$$g_{vw}^{R \rightarrow L}(E) = 4\pi^2 g_c \sum_{lr} |T_{lv, rw}|^2 \delta(E_l + \varepsilon_w - E) \delta(E_r + \varepsilon_v - E). \quad (14b)$$

In Eq. (14) the initial/final state energy has been written as the sum of the electronic (E_l , E_r) and vibrational (ε_v , ε_w) energies. Note that in general $g_{vw}^{L \rightarrow R}(E) \neq g_{vw}^{R \rightarrow L}(E)$, and, in agreement with microscopic reversibility, $g_{vw}^{L \rightarrow R}(E) = g_{vw}^{R \rightarrow L}(E)$. The identical conductance contributions in the two directions are multiplied by different Boltzmann factors and for this reason, different from the elastic case, they are considered separately. The vibronic matrix element is

$$\begin{aligned} T_{lv, rw} &= \langle \psi_l(q, Q) \Lambda_{lv}(Q) | T | \psi_r(q, Q) \Lambda_{rw}(Q) \rangle \\ &= \langle \Lambda_v(Q) | T_{lr}(Q) | \Lambda_w(Q) \rangle, \end{aligned} \quad (15)$$

where the second equality is obtained by integrating over the electronic coordinates. The indexes l, r were dropped from Λ in Eq. (15) because the two sets $\{\Lambda_{lv}\}$ and $\{\Lambda_{rv}\}$ are assumed to be identical, i.e., the molecular vibrations are not influenced by the electron being on the electrode L or R .

According to our partition of the Hamiltonian, V does not depend on the nuclear coordinate Q so that, using Eqs. (3) and (15):

$$\begin{aligned} T_{lr, vw} &= \sum_{ij} V_{li} \langle \Lambda_v(Q) | G_{ij}(E, Q) | \Lambda_w(Q) \rangle V_{jr} \\ &= \sum_{ij} V_{li} [G_{ij}(E)]_{vw} V_{jr}, \end{aligned} \quad (16)$$

$$[G_{ij}(E)]_{vw} = \langle \Lambda_v(Q) | G_{ij}(E, Q) | \Lambda_w(Q) \rangle. \quad (17)$$

To confirm the consistency of these equations we note that if T_{lr} did not depend on the nuclear coordinates or this dependence were neglected (Condon approximation) Eq. (16) would simply give $T_{lr, vw} = \delta_{vw} T_{lr}$, which substituted in Eqs. (12)–(14) gives the original expression for the purely elastic conductance.

Using Eq. (16) instead of Eq. (5) as a starting equation, we get a generalization for the vibrationally resolved conductance, separated in left to right and right to left contributions:

$$g_{vw}^{L \rightarrow R} = g_c Tr(\mathbf{\Gamma}^L(E - \varepsilon_v) \mathbf{G}_{vw}(E) \mathbf{\Gamma}^R(E - \varepsilon_w) \mathbf{G}_{vw}(E)^+), \quad (18a)$$

$$g_{vw}^{R \rightarrow L} = g_c Tr(\mathbf{\Gamma}^L(E - \varepsilon_w) \mathbf{G}_{vw}(E) \mathbf{\Gamma}^R(E - \varepsilon_v) \mathbf{G}_{vw}(E)^+). \quad (18b)$$

Matrices $\mathbf{G}_{vw}(E)$ are defined by Eq. (17).

A final expression for the conductance can be obtained after thermal averaging. This issue is complicated by the fact that many electron Fermi correlation leads to entangled initial and final states in the local representation, making it impossible to take simple thermal averages over fluxes calculated separately in the different directions.³⁶ Still, when the coupling between the left and the right Fermi seas through the molecular bridge is small we intuitively expect such av-

erages [leading to structures such as $f_L(1-f_R)+f_R(1-f_L)$ in the transport equation] to provide a reasonable approximation. This expectation is supported by model calculations⁶⁵ that show that within a reasonable range of electronic-nuclear coupling parameters the error introduced by this procedure for estimating inelastic effects in electron transmission through molecules is of the order 10–15%.

Assuming the validity of this approach the total current is written as the difference between the averaged left-to-right and right-to-left flux,

$$I = I^{L \rightarrow R} - I^{R \rightarrow L}, \quad (19)$$

$$I^{L \rightarrow R} = \int_{-\infty}^{+\infty} dE \sum_{vw} P_v(\theta) \frac{g_{vw}^{L \rightarrow R}(E)}{e} f_L(E - \varepsilon_v) \times (1 - f_R(E - \varepsilon_w)), \quad (20a)$$

$$I^{R \rightarrow L} = \int_{-\infty}^{+\infty} dE \sum_{vw} P_v(\theta) \frac{g_{vw}^{R \rightarrow L}(E)}{e} f_R(E - \varepsilon_v) \times (1 - f_L(E - \varepsilon_w)). \quad (20b)$$

The procedure followed here is reminiscent of the method used in electron spectroscopy to calculate the vibrational fine structure from the coordinate dependence of the appropriate matrix element.⁶⁶ We note that in this situation the role of vibrations is to couple different states (off-diagonal vibronic coupling) while in other approaches,^{54,55} mainly focused on the polaron formation on the wire, a diagonal Holstein-type⁵³ coupling will dominate. In contrast with polaronic analyses, the present description does not account for the formation of stable states localized on the molecule.

In principle the numerical evaluation of these formulas requires the calculation of $G(E, Q)$ over a large set of nuclear coordinates followed by the evaluation of the integral in Eq. (17). Generalization to N modes (localized on the wire) is simple, since Eqs. (11)–(20) hold if Q is interpreted as a vector of nuclear coordinates $\{Q_\alpha\}$ and v and w as vectors of quantum numbers of the various normal modes.⁶⁷ The number of matrix elements $[G_{ij}(E)]_{vw}$ to be evaluated grows exponentially with the number of modes and several approximations are conveniently set to simplify the calculation of the current and get some more physical insight.

C. Approximations

To reduce selectively the number of matrix elements $[G_{ij}(E)]_{vw}$ to be calculated we make several approximations. First we assume that the nuclear motion is harmonic. Second, we expand $G(E, \{Q_\alpha\})$ in a Taylor series around the equilibrium position $\{Q_\alpha\} = 0$. Dimensionless coordinates⁶⁸ are used for the nuclei. For a single mode we have

$$G_{ij}(E, Q) \cong G_{ij}(E, 0) + \left(\frac{\partial G_{ij}(E, Q)}{\partial Q} \right)_{Q=0} Q, \quad (21)$$

$$\begin{aligned} [G_{ij}(E)]_{vw} &= G_{ij}(E, 0) \langle \Lambda_v | \Lambda_w \rangle \\ &+ \left(\frac{\partial G_{ij}(E, Q)}{\partial Q} \right)_{Q=0} \langle \Lambda_v | Q | \Lambda_w \rangle \\ &= G_{ij}(E, 0) \delta_{vw} + \frac{\sqrt{2}}{2} \left(\frac{\partial G_{ij}(E, Q)}{\partial Q} \right)_{Q=0} \\ &\quad \times (\delta_{v, w+1} \sqrt{v} + \delta_{v, w-1} \sqrt{v+1}) \\ &\equiv G_{ij}^{(0)} \delta_{vw} + G_{ij}^{(1)} \frac{\sqrt{2}}{2} \\ &\quad \times (\delta_{v, w+1} \sqrt{v} + \delta_{v, w-1} \sqrt{v+1}). \end{aligned} \quad (22)$$

Equation (21) differs from a polaron-type analysis because it is G , and not the diagonal terms in H , that is expanded in Taylor series in Q . Physically, this means that it is the transport mechanism, not the site energies, that is vibronically modulated. Far from resonance this should be the dominant effect.⁵⁸

As expected, the first-order correction to the elastic conduction, represented by the truncated expansion in Eq. (21), is nonzero only for initial and final state differing by one vibrational quantum. For N modes $\{Q_\alpha\}$, the first derivative with respect to all Q_α must be evaluated:

$$G_{ij, \alpha}^{(1)} \equiv \left(\frac{\partial G_{ij}}{\partial Q_\alpha} \right)_{Q_\alpha=0}. \quad (23)$$

These derivatives will be calculated for several molecules in Sec. III and the ratio $G_{ij, \alpha}^{(1)}/G_{ij, \alpha}^{(0)}$ will be taken as a measure of the involvement of each mode in the electron transport. The ratio also quantifies the relative importance of inelastic versus elastic transport.

Other approximations, that may be relaxed later, are made to gain a better physical insight into the implication of Eq. (20). In the low temperature limit ($\hbar \omega \gg k_B \theta$) the wire is in its ground vibrational state and it can only gain energy from the transported electron. If the applied potential is not very high ($e\Phi \sim \hbar \omega$) and the electrodes are good metals, the values of Γ^L , Γ^R may be set to their values at the Fermi energy (E_F), neglecting their energy dependence. For the simplified wire described by Eqs. (9) and (10), this leads to

$$I = I_{\text{el}} + I_{\text{inel}}, \quad (24a)$$

where the inelastic and the elastic contributions are given by

$$I_{\text{el}} = \frac{g_c}{e} \Gamma^L(E_F) \Gamma^R(E_F) \int_{-\infty}^{+\infty} dE |G_{1N}^{(0)}|^2 [f_L(E) \times (1 - f_R(E)) - f_R(E)(1 - f_L(E))], \quad (24b)$$

$$I_{\text{inel}} = \frac{g_c}{e} \Gamma^L(E_F) \Gamma^R(E_F) \sum_{\alpha} \frac{1}{2} \int_{-\infty}^{+\infty} dE |G_{1N, \alpha}^{(1)}|^2 [f_L(E) \times (1 - f_R(E - \hbar \omega_{\alpha})) - f_R(E)(1 - f_L(E - \hbar \omega_{\alpha}))], \quad (24c)$$

where ω_{α} is the frequency of the mode α . This simple equation describes the essential physics of inelastic transport in

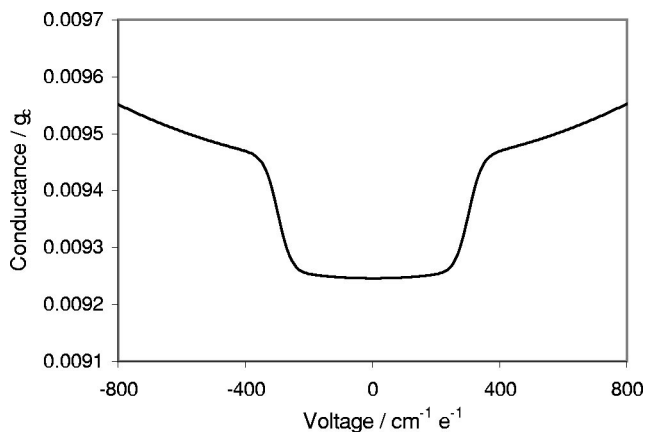


FIG. 2. Conductance (in units of quantum conductance g_c) of a model system with a single vibrational mode at 300 cm^{-1} (see the text for other details). Voltage is expressed as a difference of chemical potential (in cm^{-1}) divided by the electron charge e .

the low temperature and low potential bias regime that characterizes most experimental IETS-STM work.⁶⁹

Before discussing some realistic cases, we consider a simple model Hamiltonian, which serves as a guide in understanding the numerical results and will help the connection with other formalisms. We set the following two-states, one-vibrational-mode Hamiltonian for the molecule, with the nuclear dependence explicit in its matrix representation:

$$H(Q) = \begin{bmatrix} \varepsilon_0 + \frac{1}{2}\hbar\omega Q^2 & V_{12} + \sqrt{2}\lambda_{12}Q \\ V_{12} + \sqrt{2}\lambda_{12}Q & \varepsilon_0 + \frac{1}{2}\hbar\omega Q^2 \end{bmatrix} \quad (25)$$

and corresponding to the electronic part of the Hamiltonian expressed in second quantization as

$$H = (\varepsilon_0 + \hbar\omega(a^+a + \frac{1}{2}))(|1\rangle\langle 1| + |2\rangle\langle 2|) + (V_{12} + \lambda_{12}(a^+ + a))(|1\rangle\langle 2| + |2\rangle\langle 1|). \quad (26)$$

This model corresponds to a diatomic molecule with one orbital per site where the resonance integral V_{12} varies with the inter-nuclear distance Q . In the absence of molecular vibrations ($Q=0$) the resonant tunneling for this system would occur for $E = \varepsilon_0 \pm V_{12}$. In the off resonance situation, relevant to IETS measurements, we may disregard the self-energy terms associated with the coupling to the electrodes. We then get for the Green's function elements

$$G_{12}(E, Q) = \frac{V_{12} + \sqrt{2}\lambda_{12}Q}{(E - \varepsilon_0 - \frac{1}{2}\hbar\omega Q^2)^2 - (V_{12} + \sqrt{2}\lambda_{12}Q)^2}, \quad (27)$$

$$G_{12}^{(0)}(E) = \frac{V_{12}}{(E - \varepsilon_0)^2 - V_{12}^2}, \quad (28)$$

$$G_{12}^{(1)}(E) = \frac{\sqrt{2}\lambda_{12}}{(E - \varepsilon_0)^2 - V_{12}^2} - \frac{2\sqrt{2}\lambda_{12}V_{12}^2}{[(E - \varepsilon_0)^2 - V_{12}^2]^2}. \quad (29)$$

Equations (27)–(29) can be used to calculate a model $I(\Phi)$ curve following Eq. (24).

Figure 2 shows a plot of the conductance ($dI/d\Phi$) versus voltage given by Eqs. (24), (28), (29) for the following

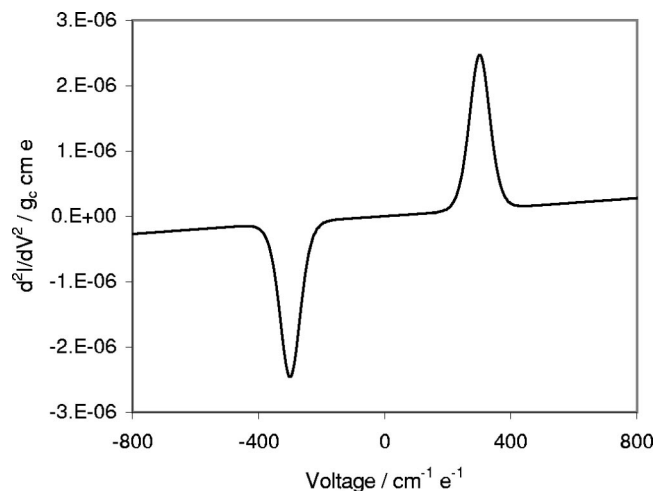


FIG. 3. Derivative of conductance for a model system with a single vibrational mode at 300 cm^{-1} . The plot is a model for the IETS-STM measurements.

set of parameters $\varepsilon_0 = 0\text{ cm}^{-1}$, $V_{12} = 10000\text{ cm}^{-1}$, $\lambda_{12} = 500\text{ cm}^{-1}$, $\hbar\omega = 300\text{ cm}^{-1}$, $\Gamma^R = \Gamma^L = 1000\text{ cm}^{-1}$, $\theta = 20\text{ K}$. A conductance jump is observed at voltage (or electrochemical potential difference) 300 cm^{-1} where the inelastic channel becomes active. The corresponding second derivative, $d^2I/d\Phi^2$ depicted in Fig. 3, shows a peak whose intensity is related to the electronic–nuclear coupling while its width is temperature dependent and derives from the Fermi functions in Eq. (24). Figure 3 is a model for the experimentally observed IETS spectra,⁴⁹ which also show a jump in the conductance.

It is also interesting, for the analysis which follows, to consider the ratio $G_{ij,\alpha}^{(1)}/G_{ij,\alpha}^{(0)}$ as a measure of the relative importance of the inelastic versus elastic conduction. Using Eqs. (28) and (29) this is

$$\frac{G_{12}^{(1)}(E)}{G_{12}^{(0)}(E)} = \frac{\sqrt{2}\lambda_{12}}{V_{12}} - \frac{2\sqrt{2}\lambda_{12}V_{12}}{(E - \varepsilon_0)^2 - V_{12}^2}. \quad (30)$$

We note that for large $|E - \varepsilon_0|$ the ratio does not depend on this energy difference, i.e., is not associated with the transversal time for tunneling,^{70,71} suggested to monitor the time the electron spends in the barrier region. This results from the fact that in the present model the electron–nuclear interaction modifies the electronic interstate coupling and cannot be regarded as a local on-bridge property. Mathematically this appears in the fact that the elastic and inelastic interactions (V_{12} and λ_{12}) appear in the same (first) order in the interstate coupling.

III. CALCULATIONS AND DISCUSSION

A. Computational model

The method described in Sec. II will be applied for calculating the relevant vibronic coupling for four molecules (see Fig. 1) often considered as prototypes for molecular wires:^{72–74} butadiene, biphenyl, dipyrrole (*trans* conformation) and dithiophene (*trans* conformation). We use the Hartree–Fock (HF) method in its *ab initio* implementation to define the molecular one-electron effective Hamiltonian for

Eq. (1), which is then effectively replaced by the Fock operator.²⁷ Alternatively one can use a DFT approach.

The calculation of molecular conductance involves (i) a suitable electronic structure calculation, (ii) identification of the correct junction geometry, (iii) calculation of self-energy terms, and (iv) a determination of the relative positions of the Fermi energy and molecular levels. These issues require the computationally intensive combination of structural optimization and conductance calculation at each voltage *for each specific junction* determined by the geometry and the nature of the molecule–metal interfaces. In our present first application we focus on the inelastic conductance by the given molecule, disregarding details of the molecule–metal interaction. To this end we will use a model where Eqs. (9) and (10) are valid, i.e., molecule coupled to metal only through two terminal atomic orbitals. In this case Eq. (24) is valid and the inelastic versus elastic contribution may be evaluated without the explicit calculation of the self-energy (Γ^L , Γ^R) matrices. On this level of treatment, inelastic effects on the molecular conduction are not influenced by other details of the model system. Moreover, it facilitates obtaining propensity rules for involvement of various nuclear modes in the electron transport, expressed as intrinsic molecular properties, although they may be somewhat modulated by the metal electrodes in any specific junction.⁷⁵

For the four considered molecules, the “contact orbitals” [$|1\rangle$ and $|N\rangle$ in Eq. (24)] are taken to be the p_z orbitals on the carbon atoms at the molecular edges as indicated in Fig. 1. The 6-31G(*d*) basis set was used in the HF calculations. The optimized geometry and the normal modes have been calculated at the same level.⁷⁶ The matrix representing the molecular Green’s function in the nonorthogonal metric⁷⁷ is

$$\mathbf{G}(E) = \mathbf{S}(\mathbf{S}E - \mathbf{F})^{-1}\mathbf{S}, \quad (31)$$

where \mathbf{S} is the overlap matrixes in the atomic set and \mathbf{F} is the Fock matrix. Self-energy terms due to the metal were not included. Their potential role on the inelastic tunneling is discussed in Sec. III B.

The derivatives $\partial G_{1N}/\partial Q_\alpha$ were calculated numerically with a displacement of 0.01 dimensionless units for all the symmetric modes. For the four considered molecules, in fact, only totally symmetric modes have $G_{1N,\alpha}^{(1)}$ different from zero. Defining the symmetrized combinations $|\lambda_+\rangle = (|1\rangle + |N\rangle)/2$ and $|\lambda_-\rangle = (|1\rangle - |N\rangle)/2$ we therefore get

$$\langle 1 | \frac{\partial G}{\partial Q_\alpha} | N \rangle = \langle \lambda_+ | \frac{\partial G}{\partial Q_\alpha} | \lambda_+ \rangle - \langle \lambda_- | \frac{\partial G}{\partial Q_\alpha} | \lambda_- \rangle, \quad (32)$$

which is nonzero only if Q_α is totally symmetric (because G is totally symmetric). However some calculations on the other modes have been performed to assure that the error introduced by the numerical derivative negligibly affects the results. The GAMESS package⁷⁸ was employed to perform the quantum chemical calculations.

Results of these calculations are presented in terms of the ratios [using the definition of Eqs. (21) and (22)]:

$$R_{1N,\alpha}(E) \equiv \frac{G_{1N,\alpha}^{(1)}(E)}{G_{1N}^{(0)}(E)}, \quad (33)$$

TABLE I. Contribution of the butadiene a_g modes to the inelastic conduction expressed in terms of $R_{1N,\alpha}$ [defined by Eq. (33)].

a_g mode	Frequency (cm ⁻¹)	$R_{1N,\alpha}(E=0) \times 10^2$ ^a
1	550.2	1.5
2	959.4	4.6
3	1325.5	-8.3
4	1435.3	2.9
5	1613.5	-4.9
6	1897.7	-16.0
7	3325.4	-1.6
8	3342.6	-1.0
9	3414.3	-0.8

^a $G_{1N}^{(0)} = 1.8359$ hartree⁻¹.

which express the relative importance of inelastic transport induced by mode α with respect to the elastic one. Values of $R_{1N,\alpha}(E)$ together with $G_{1N}^{(0)}(E)$ can be used to simulate IETS spectra according to Eq. (24), as has been done with the model Hamiltonian. The values of $R_{1N,\alpha}(E)$ will be discussed for $E=0$ a.u., an energy close to halfway between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as the Fermi energy of a generic metal. The energy dependence of $R_{1N,\alpha}(E)$ will be discussed in the following.

B. Vibronic coupling calculation

Table I collects the value of $R_{1N,\alpha}(E)$ for all the totally symmetric modes of butadiene at $E=0$ a.u. The mode that gives the largest contribution to the inelastic conduction is the C=C stretching of the double bond (mode $6a_g$, Fig. 4). This is largely expected, since the C–C stretching is the unique mode included in common models of polaron diffusion in polyenes.⁵⁶ From our calculation however, the contribution of the mixed C–C–H and C–C–C bending (modes $2a_g$, $3a_g$) turns out to be not negligible and of similar importance as the other C–C stretching (mode $5a_g$). The overall inelastic contribution to the conductance, estimated from $|R_{1N,\alpha}|^2$, is close to 1.5%⁷⁹ at small bias.

The energy dependence of $R_{1N,\alpha}(E)$ for mode $6a_g$ is displayed in Fig. 5. $R_{1N,\alpha}(E)$ is approximately constant for a wide range of energies between the HOMO and the LUMO energies, however it shows a typical resonance increase near these energies (similar results are found for all the active modes). If no-self energy term is included $R_{1N,\alpha}(E)$ diverges near these poles in the Green’s function, therefore addressing such resonance effects requires a calculation of self-energies

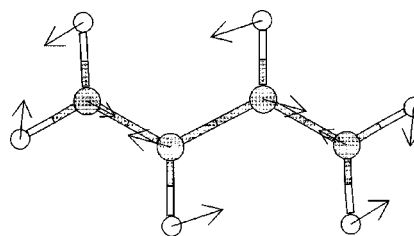


FIG. 4. Illustration of normal mode $6a_g$ of the butadiene that gives the greatest contribution to the inelastic conductance.

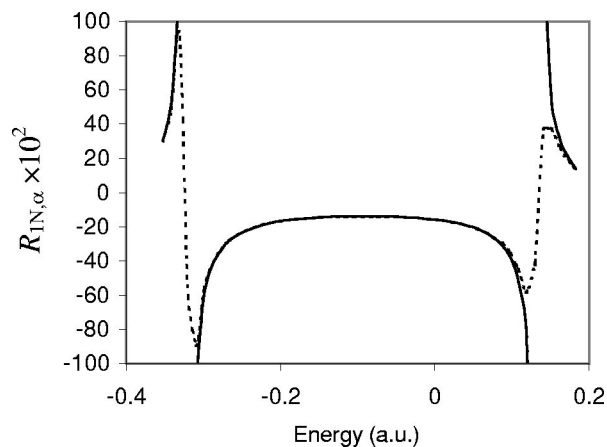


FIG. 5. Energy dependence of $R_{1N,\alpha}(E)$ for mode $6a_g$ of butadiene. Solid line: Self-energy is neglected (set to zero). Dashed line: the imaginary part of the self-energy, set to 2000 cm^{-1} , was added to the diagonal elements of the molecular Hamiltonian corresponding to the orbitals in contact with the leads.

such as done, for example, in Ref. 29. The curve in Fig. 5 is the numerical counterpart of the analytical expression of Eq. (30), which can model almost perfectly the computational results. This result indicates that Table I and the analogous Tables II–IV are representative results for a generic off-resonance injection energy in the HOMO–LUMO gap. It is remarkable that, although the total current is strongly dependent on the relative position of the Fermi energy and the molecular levels, the inelastic fraction of the current is substantially independent of these parameters in the off-resonance regime. Another important consequence of the result illustrated by Fig. 5 is that the imaginary component of the self-energy, which determines the absolute values of the current and enters in the denominator of the Green's function, has a negligible effect on $R_{1N,\alpha}(E)$ in the off-resonance regime.

An analogous calculation for biphenyl is presented in Table II. Figure 6 displays some of the normal modes with

TABLE II. Contribution of the biphenyl a modes to the inelastic conduction expressed in terms of $R_{1N,\alpha}$.

a mode	Frequency (cm^{-1})	$R_{1N,\alpha}(E=0) \times 10^2$ ^a
1	67.7	8.6
2	330.3	−1.4
3	461.5	−7.3
4	807.3	−2.8
5	960.3	−3.6
6	1089.2	4.2
7	1104.6	−1.3
8	1133.0	4.0
9	1306.9	−6.9
10	1405.6	−7.2
11	1683.3	0.5
12	1815.4	20.9
13	3353.9	−1.5
14	3374.5	−2.5
15	3389.4	0.6

^a $G_{1N}^{(0)} = 0.4245 \text{ hartree}^{-1}$.

TABLE III. Contribution of the dipyrrole a modes to the inelastic conduction expressed in terms of $R_{1N,\alpha}$.

a mode	Frequency (cm^{-1})	$R_{1N,\alpha}(E=0) \times 10^2$ ^a
1	65.5	12.8
2	130.6	−7.5
3	411.2	−0.8
4	463.3	3.1
5	525.9	−2.7
6	677.1	7.0
7	724.8	−0.7
8	821.7	3.3
9	898.9	−0.9
10	963.8	−1.9
11	989.8	−3.1
12	1058.8	0.1
13	1125.0	9.4
14	1207.2	1.3
15	1240.1	−2.3
16	1396.8	−1.7
17	1416.6	3.6
18	1580.4	10.2
19	1616.1	5.4
20	1658.6	12.7
21	1821.1	−13.1
22	3414.4	−0.5
23	3430.2	−1.4
24	3454.6	1.3
25	3917.6	−2.4

^a $G_{1N}^{(0)} = 0.3980 \text{ hartree}^{-1}$.

relatively large values of $R_{1N,\alpha}(E)$. Many modes give appreciable contribution to the inelastic current and, as generally happens with vibronic coupling calculations,⁸⁰ it is not possible to fully rationalize these results only by chemical intu-

TABLE IV. Contribution of the dithiophene a modes to the inelastic conduction expressed in terms of $R_{1N,\alpha}$.

a mode	Frequency (cm^{-1})	$R_{1N,\alpha}(E=0) \times 10^2$ ^a
1	41.6	6.7
2	121.1	2.2
3	307.0	0.4
4	396.9	−1.1
5	513.7	3.0
6	620.4	−4.8
7	735.6	−1.9
8	804.4	0.0
9	806.4	−0.6
10	925.3	4.2
11	960.1	2.3
12	1048.6	−0.1
13	1133.2	−8.7
14	1210.8	3.0
15	1337.3	0.6
16	1399.1	1.2
17	1522.9	4.2
18	1649.4	25.6
19	1781.5	12.7
20	3393.4	−1.3
21	3408.1	−0.2
22	3443.1	2.5

^a $G_{1N}^{(0)} = 0.6109 \text{ hartree}^{-1}$.

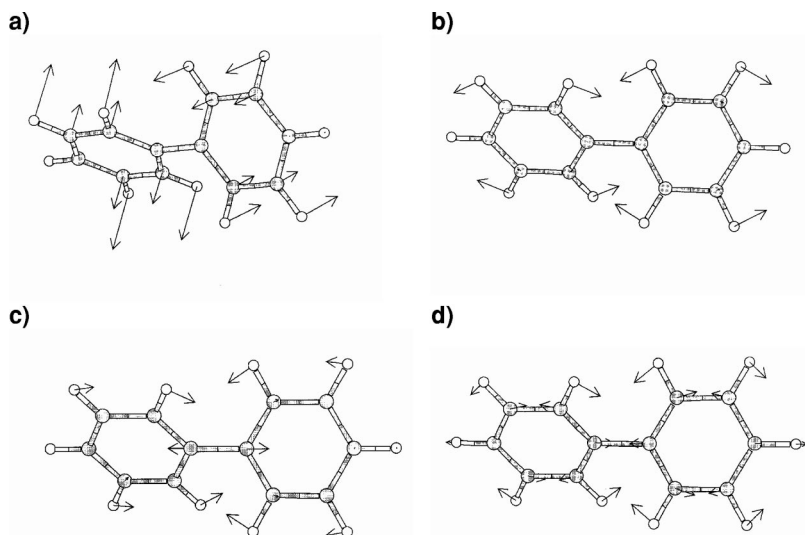


FIG. 6. Illustration of some of the normal modes of biphenyl that give a greater contribution to the inelastic conductance (Table II); (a) mode 1a; (b) mode 9a; (c) mode 10a; (d) mode 12a.

ition. However, several points may be noticed. As in the butadiene case, the greatest contribution is associated with the C=C stretching mode [12a, Fig. 6(d)], which also gives a 2% relative contribution to the total conductance. Another important contribution comes from other C=C stretching modes (9a, 10a) mixed with the C-C-H bending. As expected, the contribution of the inter-ring torsion [mode 1a, Fig. 6(a)] is also relevant. The contribution of this mode may be influenced by the equilibrium position of the inter-ring dihedral angle (45.5° in our calculations) and may therefore change more significantly with the level of calculation.⁸¹ The C-H stretching modes expectedly give the smallest contribution.

Values of $R_{1N,\alpha}(E)$ for dipyrrole and dithiophene are shown in Tables III and IV, and some modes for the dipyrrole are illustrated by Fig. 7. These results may be rationalized in a way similar to that used for the biphenyl. A C=C stretching mode gives the highest contribution (mode 21a for dipyrrole and 18a for dithiophene), followed by other C-C stretching combinations and by a more complex combination of C-C-H and C-C-C bending. Inter-ring torsion (mode

1a) is also very important especially in the dipyrrole case. The pattern of the inelastic contributions of these two molecules is very similar despite the different heteroatoms. The tunneling, in fact, is mainly affected by the vibrations that influence the C-C conjugation pattern and that do not involve the heteroatom. The total inelastic contribution is close to 5% for both molecules.

The harmonic approximation is sufficiently accurate for these molecules at low temperature ($\hbar\omega \gg k_B\theta$) when the wire does not undergo conformational changes and it is close to its equilibrium geometry. For higher temperature, the low energy modes are excited and anharmonic effects are expected to be important for some of the modes, in particular those involved in potential conformational changes. For the two-ring systems considered here, the torsion around the inter-ring bond clearly cannot be considered harmonic at room temperature (rotational barriers are around $100\text{--}400\text{ cm}^{-1}$) and the $[G_{1N}]_{vw}$ matrix element for this mode must be calculated from Eq. (17) using the anharmonic wave functions. In general, for realistic systems at high temperature few low frequency modes may be considered anharmonic,

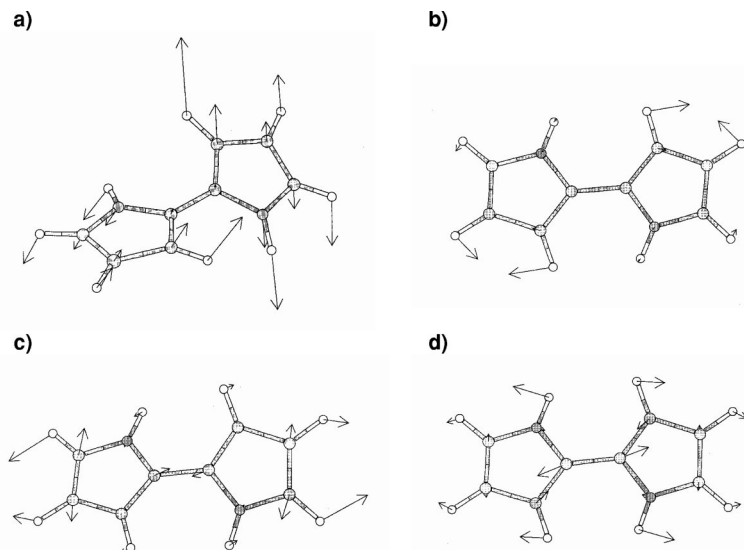


FIG. 7. Illustration of some of the normal modes of dipyrrole that give a greater contribution to the inelastic conductance (Table III); (a) mode 1a; (b) mode 13a; (c) mode 20a; (d) mode 21a.

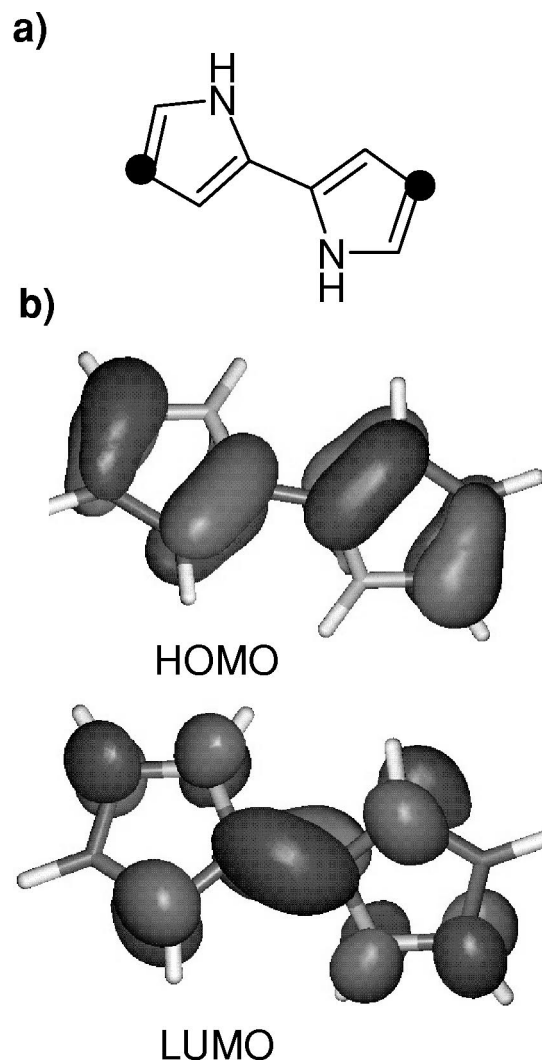


FIG. 8. (a) Black circles show the alternative choice of contact atoms for dipyrrole made in Sec. III C. (b) The frontiers orbitals of dipyrrole showing a nodal plane crossing the contact atoms in the LUMO.

while for the others Eqs. (21) and (22) may be conveniently used. We note that, at higher temperature, other conformations became accessible and the effect of nuclear motion on conductance becomes primarily an issue of conformational averaging as shown in several recent experiments.^{52,82}

C. Electronically forbidden electron transport

In the examples analyzed so far the relative inelastic contribution to the current was not very high and may be thought of as a correction to the first-order picture dominated by the elastic transport. However, when electronic coupling in the equilibrium geometry is very low or is zero (we loosely refer to this situation as *electronically forbidden electron transport*), the contributions of different conformations as well as inelastic transmission is expected to be decisive.

A simple example of electron transport strongly induced by the nuclear motions can be found by reconsidering the dipyrrole molecule but changing the atoms in contact with the metal to those illustrated in Fig. 8(a). Table V shows the R ratios, recomputed for this apparently marginal change in the structure of the junction. The total inelastic contribution

TABLE V. Contribution of the dipyrrole α modes to the inelastic conduction expressed in terms of $R_{1N,\alpha}$. The contact orbitals are the ones depicted in Fig. 8(a). The frequencies are the same as in Table IV.

α modes	$R_{1N,\alpha}(E=0) \times 10^2$ ^a
1	82.9
2	3.1
3	1.0
4	-29.2
5	8.2
6	-3.0
7	-5.3
8	-15.4
9	15.7
10	16.9
11	0.9
12	-1.5
13	8.2
14	48.5
15	-8.7
16	-7.8
17	-21.9
18	-35.7
19	19.9
20	27.4
21	-13.5
22	-8.6
23	3.7
24	5.8
25	-2.8

^a $G_{1N}^{(0)} = 0.02166 \text{ hartree}^{-1}$.

from all modes is now greater than the purely elastic one, in particular the inter-ring torsional mode induces a current comparable to the elastic one. The reason for this huge effect can be readily found considering the HOMO and LUMO nodal planes in the dipyrrole molecules [depicted in Fig. 8(b)]. Most of the current in the low bias off-resonance regime is due to the superexchange interaction of these orbitals with the metals. A nodal plane of the LUMO crosses the atoms in contact with the metals and the elastic contribution through the LUMO channel is almost zero. As a consequence, $G_{1N}^{(0)}$ is lower than the other cases (see Table V) and the ratio $R_{1N,\alpha}$ will be particularly high especially at energies closer to LUMO energy.

The observation of electronically forbidden electron transfer induced by local distortion or by the intervening solvent was made by several authors.⁸³⁻⁸⁵ We argue that such mechanisms may be active also in molecular wires when the coupling is not particularly effective. Note that we have assumed that the molecular geometry (and symmetry) does not change in the junction. In fact such conformational changes induced by the molecule-metal binding may be important in the induction of electron transport in such situations.

IV. CONCLUSION

We have presented a model for the calculation of the inelastic contribution to the electrical conduction in molecular wires. The model has been designed to be used in connection with *ab initio* calculations, where a suitable cluster models the metal-molecule-metal junction. We applied the model to the calculation of the inelastic contribution to the

conductance for several molecules usually taken as models of molecular wires. The main achievement of this work is the quantification of such contributions obtained without using empirical parameters. For several specific systems the molecular vibrations that play a major role in promoting the induction of inelastic transport are identified and, for the molecules considered, they are rationalized according to simple propensity rules. The model is potentially useful when the electronic coupling between the donor and acceptor species is small in the equilibrium configuration. In such cases vibronic interactions may play a dominant role, as illustrated by one of the considered examples. These general considerations apply both for molecular wires and in situations where the molecules act as bridges between donor and acceptor species.

The model, including the approximations done in Sec. II B, has been designed for the study of the off-resonant situations. In this limit inelastic contributions were shown to be nearly independent of the position of the molecular HOMO and LUMO. In the opposite limit of near resonance transmission, the expansion of Eq. (21) cannot be used and exact evaluation of the vibronic matrix element is needed. Moreover, in this resonance regime, aspects that are not included in the present model such as charging of the molecule and sequential transport become extremely important and our description should be complemented by other considerations.

While our model was based on a general formulation, we have made a series of subsequent approximations that can be selectively relaxed. A subject of current investigation is the effect of large amplitude motions on the molecular electric conduction. This requires the inclusion of anharmonic effects and calls for a deeper understanding of the temperature role. An improvement of the molecular junction model to include several atoms of the metallic contact will also clarify the role of the molecule-metal bond on the inelastic conduction.

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