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Inelastic scattering in metal-H_2-metal junctions

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We present first-principles calculations of the dI/dV characteristics of an H_2 molecule sandwiched between Au and Pt electrodes in the presence of electron-phonon interactions. The conductance is found to decrease by a few percentages at threshold voltages corresponding to the excitation energy of longitudinal vibrations of the H_2 molecule. In the case of Pt electrodes, the transverse vibrations can mediate transport through otherwise nontransmitting Pt d channels leading to an *increase* in the differential conductance even though the hydrogen junction is characterized predominately by a single almost fully open transport channel. In the case of Au, the transverse modes do not affect the dI/dV because the Au d states are too far below the Fermi level. A simple explanation of the first-principles results is given using scattering theory. Finally, we compare and discuss our results in relation to experimental data.

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In recent years it has become possible to measure the electrical properties of single molecules captured between metallic electrodes.[1–3] Such experiments provide a unique opportunity to develop our understanding of basic quantum-mechanical phenomena at the nanometer length scale and at the same time constitute the first steps toward molecule-based electronics.[4]

Interactions between the conduction electrons and the molecule's vibrational degrees of freedom is of particular interest for the performance of molecular electronics devices as they determine the local temperature and stability of the device when subject to an external bias voltage.[5] Moreover, inelastic scattering can be used to identify the atomic structure of molecular junctions by exploiting the sensitiveness of the molecule's vibrational frequencies and the electron-phonon interaction to the junction geometry.[6–12]

Perhaps the simplest molecular junction consists of a single hydrogen molecule sandwiched between metal electrodes; see Fig. 1.[3,13] Shot noise measurements on Pt-D_2 contacts show that the conductance is carried predominantly by a single almost fully transparent channel,[14] and density-functional theory (DFT) calculations have shown that this is consistent with a linear bridge configuration.[3,15–17] An alternative configuration where the H_2 molecule is dissociated in the contact has also been proposed, however, this junction yields a conductance larger than $1G_0$ ($G_0=2e^2/h$ is the conductance quantum) with contributions from three channels.[18] Inelastic point-contact spectroscopy provides information about the hydrogen molecule's vibrational frequencies and their variation upon stretching. The data obtained from such measurements have also been found to be consistent with the linear bridge configuration.[7]

The fact that the hydrogen junction supports a single, almost fully open conductance eigenchannel suggests that the inelastic-scattering processes should be particularly simple to understand. Indeed, consider a junction supporting a single-scattering channel at the Fermi energy with a transmission probability of $\mathcal{T}=|t(\varepsilon_F)|^2$. At low temperatures the molecule sits in its vibrational ground state and the electron looses the energy $\hbar\Omega$ to the molecule during a scattering event. Assuming a bias voltage $eV=\mu_L-\mu_R>\hbar\Omega$ an electron incident on the molecule from the left with an energy just below μ_L, must end up in a left moving scattering state after interacting with the molecule. This follows from energy conservation and the Pauli principle. Upon inelastic scattering, the probability for the electron to enter the right electrode is thus changed from $\mathcal{T}$ to $\mathcal{R}=1-\mathcal{T}$. Consequently, the change in conductance due to the electron-phonon interaction should be proportional to $2\mathcal{T}-1$, i.e., an increase (decrease) in the conductance is expected for $\mathcal{T}<0.5$ ($\mathcal{T}>0.5$). The same conclusion has been reached using more rigorous arguments[19–21] and has recently been supported by measurements on Pt-H_2O junctions.[22]

In this paper we present DFT calculations for the dI/dV curves of Pt-H_2-Pt and Au-H_2-Au junctions in the presence of electron-phonon interactions. For both Pt and Au electrodes, scattering on the longitudinal modes lowers the conductance by a few percentage of G_0 in accordance with the simple one-channel model discussed above. In the case of Pt, the transverse modes can mediate tunneling through the oth-

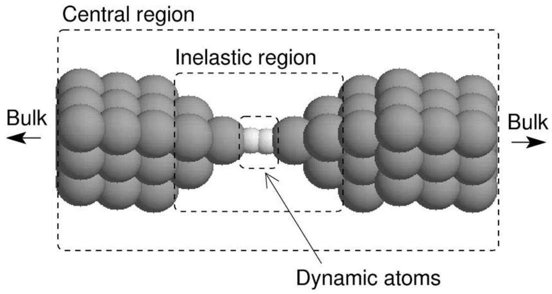

FIG. 1. The supercell use to model the metal-H_2-metal junction. Only the hydrogen atoms are allowed to vibrate (the "dynamic" atoms). This is a good approximation due to the large difference in mass between Au/Pt and H. The effect of the field generated by the vibrating H atoms is taken into account inside the indicated inelastic region. The central region, C, is coupled to semi-infinite bulk electrodes and periodic boundary conditions are imposed in the directions perpendicular to the contact axis.

erwise closed d-channels leading to an *increase* in the conductance of up to 5% of G_0, demonstrating that the metal-H_2-metal junction cannot be viewed as a simple one-channel system. For Au, the transverse modes have no effect on the conductance because only s states are present at the Fermi level and these do not couple via the transverse vibrations.

The Hamiltonian of the system is given by

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}}, \tag{1}$$

where $\hat{H}_{\text{el}}$ is the Hamiltonian of electrons moving in the *static* equilibrium structure, $\hat{H}_{\text{ph}}$ describes the vibrations of the H_2 molecule, and $\hat{H}_{\text{el-ph}}$ is the interaction between the electrons and the vibrating hydrogen atoms. For $\hat{H}_{\text{el}}$ we use the Kohn-Sham Hamiltonian.

Within the harmonic approximation the molecular vibrations are described by the Hamiltonian $\hat{H}_{\text{ph}}=\Sigma_\lambda \hbar\Omega_\lambda(b_\lambda^\dagger b_\lambda+\frac{1}{2})$ where $b_\lambda^\dagger$ (b_λ) creates (destroys) a phonon in mode λ. The electron-phonon interaction takes the form

$$\hat{H}_{\text{el-ph}} = \sum_{n,m\in C}\sum_{\lambda} M_{nm}^{\lambda} c_n^\dagger c_m (b_\lambda^\dagger + b_\lambda), \tag{2}$$

where the first sum runs over Wannier functions located in the inelastic region, see Fig. 1, and the second sum runs over vibrational modes. The electron-phonon coupling matrix, M^λ, is given by $M_{nm}^\lambda=\langle\phi_n(\mathbf{r})|W^\lambda(\mathbf{r})|\phi_m(\mathbf{r})\rangle$, where the displacement potential, $W^\lambda(\mathbf{r})=\nabla v_s[\{\mathbf{R}_n\}](\mathbf{r})\cdot\mathbf{Q}_\lambda$, is the derivative of the effective KS potential in the direction defined by eigenmode λ. In practice W^λ is obtained as a finite difference between equilibrium Hamiltonians describing the electronic system when the hydrogen molecule has been moved in the positive and the negative normal direction.

The current flowing into the molecule (central region C) from lead $\alpha=L,R$ is calculated from the formula[23,24]

$$I_\alpha = \frac{e}{h}\int \mathrm{Tr}[\Sigma_\alpha^<(\varepsilon)G_C^>(\varepsilon) - \Sigma_\alpha^>(\varepsilon)G_C^<(\varepsilon)]d\varepsilon, \tag{3}$$

where $G_C^{<,>}$ is the lesser and greater Green's functions of the central region evaluated in the presence of coupling to leads and the phonons.[25]

The lesser and greater Green's functions are given by

$$G^{\lessgtr}(\varepsilon) = G^r(\varepsilon)[\Sigma_L^{\lessgtr}(\varepsilon) + \Sigma_R^{\lessgtr}(\varepsilon) + \Sigma_{\text{ph}}^{\lessgtr}(\varepsilon)]G^a(\varepsilon), \tag{4}$$

where $G^r(\varepsilon)=[\varepsilon+i\eta-[H_{\text{el}}]_C-\Sigma_L^r-\Sigma_R^r-\Sigma_{\text{ph}}^r]^{-1}$ and $G^r(\varepsilon)=[G^a(\varepsilon)]^\dagger$.

The self-energy originating from the coupling to the leads are calculated using standard techniques.[26] For the self-energy due to the electron-phonon coupling from mode λ we use the first Born approximation,

$$\Sigma_{\text{ph},\lambda}^{\lessgtr}(\varepsilon) = M^\lambda G_0^{\lessgtr}(\varepsilon \pm \hbar\Omega_\lambda)M^\lambda \tag{5}$$

$$\Sigma_{\text{ph},\lambda}^r(\varepsilon) = \frac{1}{2}[\Sigma_{\text{ph},\lambda}^>(\varepsilon) - \Sigma_{\text{ph},\lambda}^<(\varepsilon)] - \frac{i}{2}\int \frac{\Sigma_{\text{ph},\lambda}^>(\varepsilon') - \Sigma_{\text{ph},\lambda}^<(\varepsilon')}{\varepsilon - \varepsilon'}d\varepsilon', \tag{6}$$

where the last equation follows from the general identity $G^r - G^a = G^> - G^<$ together with the Kramer's Kronig relation between Im Σ^r and Re Σ^r. We assume zero-phonon temperature corresponding to infinite cooling of the vibrations, and thus the number of phonons has been set to zero. Consequently electrons never interact with an excited molecule and therefore can only lose energy to the molecule during a scattering event.

As done often we have omitted the Hartree term in the electron-phonon self-energy.[27,28] The corresponding energy-independent contribution to the retarded self-energy can be understood as a static phonon-induced change in the mean-field electronic potential. It is expected that this small static potential would be, at least partially, screened if included in the DFT self-consistency loop.

The supercell geometry of the considered hydrogen contact is shown in Fig. 1. The distance between the two electrodes, or equivalently the length of the supercell, has for the case of Pt been chosen to make the calculated vibrational frequencies of the H_2 molecule match the experimental values as close as possible.[7] For the case of Au where less detailed experimental data is available, we have chosen the distance by minimizing the total energy. Using the plane-wave pseudopotential code Dacapo[29] we have relaxed the surface layers, the pyramids and the hydrogen molecule to obtain stable junction structures. We used an energy cutoff of 25 Ry for the plane-wave expansion, described the ion cores by ultrasoft pseudopotentials,[30] and used a $1\times4\times4$ Monckhorst pack grid for the k-point sampling. Exchange and correlation effects were described with the PW91 functional.[31] As a basis for the electronic states we use partially occupied maximally localized Wannier functions[32] which allows for an efficient and accurate calculation of transport properties as described in Ref. 26.

The vibrational eigenmodes, $\{\mathbf{Q}_\lambda\}$, and corresponding frequencies, $\{\Omega_\lambda\}$, of the H_2 molecule are obtained by diagonalizing the dynamical matrix of the system which in turn is calculated from the DFT total energies by finite differences. Thanks to the large difference in mass between the metal and hydrogen atoms, we can calculate the dynamical matrix for the two H atoms keeping all metal atoms fixed. Following this procedure we obtain a longitudinal stretching mode (M1), a longitudinal center-of-mass mode (M2), as well as two pairwise degenerate transverse modes which we refer to as hindered rotations (M3) and hindered transverse center of mass modes (M4). The modes are sketched in the insets of Fig. 2 and the corresponding frequencies are given in the caption.

In Fig. 2 we show the differential conductance calculated from Eq. (3) including scattering on the different vibrational modes separately. To extract the features due to the inelastic scattering from those due to elastic scattering we have subtracted the elastic signal, i.e., we plot $G(V)=G_{\text{full}}(V)$

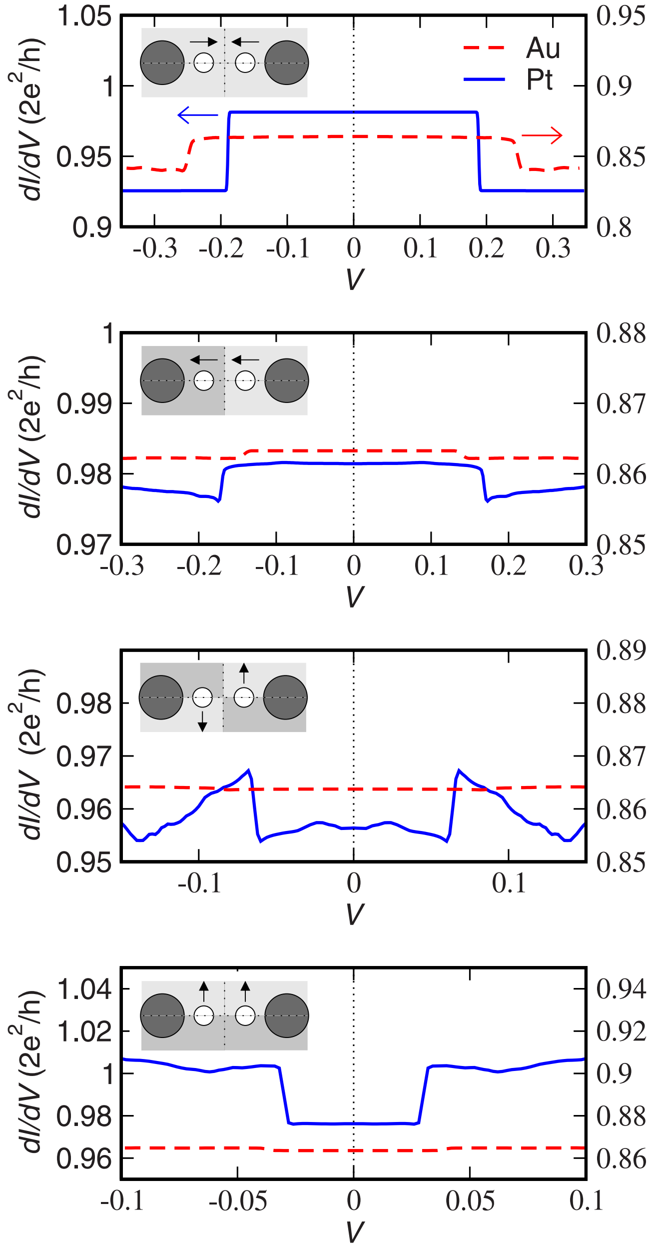

FIG. 2. (Color online) Differential conductance of the Pt-H_2-Pt (full) and Au-H_2-Au (dashed) junctions when scattering on a single vibrational mode is included. The insets illustrate the vibrational modes together with the symmetry of the corresponding displacement potential $W^{\lambda}(\mathbf{r})$. Frequencies of the H_2 vibrational modes (in meV) for Pt: $\hbar\Omega_{M1}=190$, $\hbar\Omega_{M2}=171$, $\hbar\Omega_{M3}=64$, and $\hbar\Omega_{M4}=30$ and for Au: $\hbar\Omega_{M1}=249$, $\hbar\Omega_{M2}=141$, $\hbar\Omega_{M3}=84$, and $\hbar\Omega_{M4}=37$.

$-G_{\rm el}(V)+G_{\rm el}(V=0)$, see Ref. 27 for a discussion of this procedure.

The conductance curves of Fig. 2 present several interesting features: for both Pt and Au the longitudinal modes lead to a decrease in the conductance as expected from the one-channel model. It is noticed that the internal stretching mode has a much larger impact on the electrons than the CM mode. For Au, the transverse modes have no effect on the transport, while for Pt they lead to an *increase* in the conductance. Since the junction has one fully open channel this seems to conflict with the one-channel model which would predict an increase only for junctions with conductance $<0.5G_0$. It is noted that the differences in the zero-bias conductances are due to the tails of the electron-phonon self-energy, which although centered around the vibrational frequencies also have weight at other energies. Before discussing the origin of the above mentioned features it is useful to consider a simplified description of the scattering process.

In the following we regard $\hat{H}_{\text{el-ph}}$ as a perturbation to $\hat{H}_0=\hat{H}_{\rm el}+\hat{H}_{\rm ph}$ and consider the scattering of a single electron off a molecule in its vibrational ground state. For simplicity we disregard the effect of all the other electrons (but we do take the Pauli principle into account). The scattering states of $\hat{H}_0$ are conveniently chosen as the eigenchannels incident on the molecule from the left, $\psi_{Lp}(\varepsilon)$, or right, $\psi_{Rq}(\varepsilon)$.[33,34] The probability that an electron of energy ε injected from the left lead in mode p, is transmitted (reflected) upon scattering *elastically* on the central region is denoted by $\mathcal{T}_{Lp}(\varepsilon)=|t_{Lp}(\varepsilon)|^2$ $(\mathcal{R}_{Lp}(\varepsilon)=|r_{Lp}(\varepsilon)|^2)$. Due to the nonmixing property of the eigenchannels we have $\mathcal{T}_{\alpha p}+\mathcal{R}_{\alpha p}=1$ for all channels p and $\alpha=L,R$. In terms of the eigenchannels the Landauer formula for conductance takes the form $G_{\rm el}=G_0\Sigma_p\mathcal{T}_{Lp}(\varepsilon_F)=G_0\Sigma_q\mathcal{T}_{Rq}(\varepsilon_F)$. The state of the molecule is specified by the number of phonons in each mode, $|\mathbf{n}\rangle$. We use the symbol Ψ to denote a state of the combined electron-molecule system.

Assume that $eV=\mu_L-\mu_R>0$ and consider an electron incident on the junction from the left in the state $\psi^{\rm in}=\psi_{Lp}(\varepsilon)$ with $\mu_R<\varepsilon<\mu_L$ and the molecule in its vibrational ground state, $|\mathbf{0}\rangle$. According to scattering theory, the system ends up in the asymptotic out state, $\Psi^{\rm out}=\hat{S}|Lp;\mathbf{0}\rangle$, where $\hat{S}$ is the scattering operator incorporating the effect of $\hat{H}_{\text{el-ph}}$. In the first Born approximation we have the transition amplitudes

$$\begin{aligned}\langle \alpha q;\mathbf{n}|\hat{S}|Lp;\mathbf{0}\rangle &\approx \langle \alpha q;\mathbf{n}|Lp;\mathbf{0}\rangle - 2\pi i\,\delta(E_{\rm in}-E_{\rm out})\\ &\quad\times\langle \alpha q;\mathbf{n}|\hat{H}_{\text{el-ph}}|Lp;\mathbf{0}\rangle,\end{aligned}\tag{7}$$

where $E_{\rm in}$ and $E_{\rm out}$ are the total energies of the combined electron phonon system in the in- and out-going states. This allows us to express the out state as

$$\Psi^{\rm out}=C_p\left[\psi_{Lp}(\varepsilon)\otimes|\mathbf{0}\rangle+\sum_{q,\lambda}{}'c^{\lambda}_{pq}\psi_{Rq}(\varepsilon-\hbar\Omega_{\lambda})\otimes|1_{\lambda}\rangle\right],\tag{8}$$

where the prime in the sum means that only modes with $\hbar\Omega_{\lambda}<eV$ are included. The expansion coefficients are

$$c^{\lambda}_{pq}=D_{Rq}(\varepsilon-\hbar\Omega_{\lambda})\langle\psi_{Rq}(\varepsilon-\hbar\Omega_{\lambda})|W^{\lambda}(\mathbf{r})|\psi_{Lp}(\varepsilon)\rangle,\tag{9}$$

where $D_{Rq}(\varepsilon)$ is the electronic density of states for channel Rq. The normalization constant, $C_p=(1+\Sigma'_{q,\lambda}|c^{\lambda}_{pq}|^2)^{-1/2}$, has been introduced because the first Born approximation is not a unitary approximation to $\hat{S}$. The fact that only states coming from the right electrode are included in the sum of Eq. (8) is a simple consequence of the Pauli principle.

In the elastic case, an electronic wave-packet constructed from the states ψ_{Lp} in a narrow interval around the energy ε, initially located far from the molecule in the left lead, will make it to the right lead with probability $\mathcal{T}_{Lp}(\varepsilon)$. In contrast the scattered state (8) describes a situation where the initial wave packet makes it to the right electrode with probability

$$P_p = |C_p|^2 \left[\mathcal{T}_{Lp}(\varepsilon_F) + \sum_{q,\lambda}{}' |c^{\lambda}_{pq}|^2 \mathcal{R}_{Rq}(\varepsilon_F) \right], \qquad (10)$$

where we have assumed that $\mathcal{T}$ and $\mathcal{R}$ varies little on the scale of $\hbar\Omega$. The total change in conductance due to the inelastic scattering can then be obtained from Landauer's formula

$$\Delta G = G_0 \sum_p |C_p|^2 \sum_{q,\lambda}{}' |c^{\lambda}_{pq}|^2 [\mathcal{R}_{Rq}(\varepsilon_F) - \mathcal{T}_{Lp}(\varepsilon_F)]. \qquad (11)$$

Apart from the assumptions of instantaneous cooling of the phonons and weak electron-phonon interaction, which also underlie the first-principles results, Eq. (11) was derived in the absence of a Fermi sea. However, as we show below, Eq. (11) provides a simple and physically appealing explanation of the first-principles results of Fig. 2.

It follows from Eq. (11) that the change in conductance involves all pairs of channels for which the matrix element $\langle \psi_{Lp} | W^{\lambda}(\mathbf{r}) | \psi_{Rq} \rangle$ is nonzero for some mode λ. Since $W^{\lambda}(\mathbf{r})$ extends to the metal atoms binding to H_2, any scattering state—transmitting or not—with weight on these atoms will also contribute in Eq. (11).

In the case of Pt, we find at the Fermi level two types of eigenchannels with sufficient weight on the hydrogen atoms and the contacting Pt atoms that the coupling matrix element will be significant. One eigenchannel is the almost fully open *s* channel and the others have *d* character and very low transmission at ε_F. Since Au has no *d* states at the Fermi level, only the *s* channel makes a contribution in Eq. (11).

For the longitudinal modes, M1 and M2, the symmetry of W^{λ} implies that *s*-*s* transitions are possible, but not *s*-*d* transitions (*d*-*d* transitions are not excluded by symmetry, but because of the vanishing overlap between ψ_{Ld} and ψ_{Rd}). Since $\mathcal{R}_s - \mathcal{T}_s \approx -1$ we should expect a drop in conductance in agreement with the first-principles calculations. On the hydrogen molecule, the *s* channel has mainly character of the H_2 antibonding orbital. This implies that the product $\psi_{Ls}(\mathbf{r})^* \psi_{Rs}(\mathbf{r})$ is unchanged upon reflection in the plane cutting through the H-H bond perpendicular to the molecular axis. On the other hand the potential $W^{M2}(\mathbf{r})$ changes sign upon this reflection. Consequently, the matrix element $\langle \psi_{Rs} | W^{M2} | \psi_{Ls} \rangle$ will be almost zero, and this explains the weak signal observed for M2 as compared to M1.

The spatial shape of the *d* states implies that coupling to the *s* channel is possible only via the transverse modes M3 and M4, see the symmetry of W^{λ} in the insets of Fig. 2. Limiting the sums in Eq. (11) to these two relevant states we see that ΔG becomes proportional to $\mathcal{R}_d - \mathcal{T}_s$. The increase in conductance found for the transverse modes in the Pt contact can thus be explained by a higher reflection probability of the low-transmitting *d* channel as compared to the transmission probability of the high-transmitting *s* channel. We stress that small changes in the transmission probabilities for the *s* or *d* channels could change the sign of ΔG. The symmetry of the displacement potential, W^{λ}, for the transverse modes prevents coupling between two states with *s* symmetry, which explains why the transverse modes do not affect the conductance of the Au junction.

We notice that the calculated increase in conductance due to the transverse modes is not in agreement with the experimental data from inelastic point-contact spectroscopy for Pt-H_2-Pt junctions which show a conductance decrease. Some of the possible explanations for this disagreement are:

(i) According to Eq. (11), the size (and the sign) of ΔG is determined by the relative magnitude of the *s*- and *d*-channel transmissions. Even small changes here could change the sign of ΔG. In this sense, the fact that we obtain an increase in conductance while experimentally a decrease is observed, should be viewed as a quantitative rather than a qualitative difference.

(ii) In principle the 1BA applies in the limit of weak electron-phonon interactions while we obtain electron-phonon matrix elements [M in Eq. (2)] on the order of electron volts. On the other hand the inelastic features in the dI/dV are a few percentage of G_0 indicating that only a few out of a hundred electrons are scattered. Moreover, previous studies applying the 1BA to gold chains agree nicely with experiments,[8] indicating that the 1BA provides an accurate description of electron-phonon interactions in strongly coupled metal-molecule-metal junctions.

(iii) The highly symmetric geometry of the metal-H_2-metal junction used in this study is an idealized but oversimplified model of the real structure. However, we have considered other less symmetric configurations none of which gave rise to a conductance decrease for the transverse modes.

(iv) Inclusion of a finite phonon temperature could affect the calculated properties. However, as can be seen from Eq. (14) of Ref. 35, to lowest order in the electron-phonon interaction strength the sign of ΔG cannot change by including heating.

Despite the differences between the experimental and theoretical findings for the phonon-induced features in the dI/dV, we hesitate to conclude that the linear bridge configuration is not the structure observed in the experiments. The reason is the strong evidence mentioned in the introduction which favors the linear bridge combined with the small size and high sensitivity of the inelastic features.

In conclusion, we have performed first-principles calculations for the nonlinear dI/dV curves of Pt-H_2-Pt and Au-H_2-Au molecular junctions in the presence of electron-phonon interactions. For both metals, the longitudinal vibrations of the H_2 leads to a decrease in the conductance at bias voltage corresponding to the frequency of the vibration, $eV = \hbar\Omega$. In the case of Pt electrodes, the transverse vibrations induce an increase in conductance. This might seem surprising since the hydrogen junction supports a single almost fully open transport channel and thus, according to the one-channel model, inelastic scattering should always lower the conductance. On the basis of scattering theory we showed that the increase is a result of nontransmitting *d* channels which couple to the transmitting *s* channel via the transverse modes. This is consistent with the finding that transverse modes do not affect the conductance in the case of Au electrodes.

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