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Conductance calculation of hydrogen molecular junctions between Cu electrodes

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Transport in H_2 molecules sandwiched between Cu electrodes is investigated by first principles. The theoretical results indicate the presence of two regimes characterized by high and low conductance values. Both of them comprise the molecule within the junction but differ in the adsorption geometry. An experimentally observed low conductance state is tentatively attributed to an asymmetric adsorption site at short tip-tip distances, while at longer tip-tip distances the H_2 molecule is coaxial and inside the junction, giving a conductance comparable to that of the clean contact. The threshold energy for the breakdown of the ballistic regime in the high conductance configuration is estimated as the lowest vibrational energy of the bridging H_2 molecule.

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I. INTRODUCTION

The idea of constructing single-molecule junctions and of using them in electronic devices has attracted wide attention in recent years.[1] Starting from the seminal work of Reed and coworkers,[2] several groups have reported conductance measurements of atomic scale junctions formed by metallic point contacts, individual molecules, and molecular chains.[3,4] Among all the possible molecules that could form a junction, in an intuitive picture the simplest is probably H_2.

Smith *et al.* were the first to show a single hydrogen molecule making stable contacts with Pt electrodes.[5] In their experiment, the conductance is close to 1 G_0 ($G_0 = 2e^2/h$), which is much higher than that reported for other molecular species.[6] Such a large conductance has been shown by shot-noise measurements to be originated by a single conductance channel.[7] This result, appearing as counterintuitive since resonant tunneling is not expected for a large gap system such as H_2, has stimulated theoretical studies by different authors, with debated results. Tunneling through the H_2 bonding state was put forward in Ref. 8, while Garcia *et al.* proposed an interpretation based on the claim that large conductance is due to a complex structure involving apex Pt atoms in the junctions and a dissociated H_2 molecule oriented perpendicular to the transport direction.[9] Conversely, Thygesen and Jacobsen[10] attribute the unexpected 1 G_0 conductance to a strong hybridization of the H_2 antibonding orbital and states on adjacent Pt atoms, the molecule being instead oriented along the transport direction. Their conclusions were corroborated by vibration analysis[11,12] and investigations by other groups.[13,14] The prototypical Pt/H_2/Pt junction has served also as a benchmark to test the effect of common approximations in the modeling, by including nonlocal electronic correlations and by comparing to time-dependent current-density-functional theory results.[15]

All these studies have inspired both experimentalists and theoreticians to investigate the conductance of a hydrogen molecule with electrodes of different metals, like Au,[12,16,17] Pd,[18] and magnetic 3*d* metals.[19] Results are strongly dependent on the element also within the same group, e.g., when changing from Pt to Pd the conductance lowers significantly as a result of modifications in electronic coupling between the molecule and the contact, which determines a qualitative change in the conduction mechanism near the Fermi energy.[13,14] Very recently, the case of Cu leads was studied by Kiguchi and coworkers by using the mechanically controllable break junction technique.[20] They reported a well defined peak near 1 G_0 for the clean contact (typical of atomic point contacts of *s* metals); in the presence of H_2 that peak broadens and shifts at lower values, while a second pronounced peak near 0.2 G_0 was also observed. The latter was attributed to metastable junction structures. This work raises several open questions, as well as interest in a theoretical investigation of Cu/H_2/Cu junctions, which is addressed here.

In this paper, we present first-principles calculations for the structural and transport properties of a single hydrogen molecule connecting Cu electrodes. We propose a mechanism for the interaction between the contacts and H_2, showing how the structural and transport properties vary under stretching and compression of the junction. Our models can account for the low (≈0.2 G_0) and high conductance (≈1 G_0) peaks found in the experimental histograms, highlighting that both should be addressed to molecular hydrogen junctions. We show that H_2 may be in the molecular or dissociative form, depending on the distance between the contact tips. Finally, we discuss the vibrational properties of the molecule in the junction, which can be useful to give an interpretation to inelastic electron tunneling spectroscopy. The paper is organized as follows. In Sec. II the theoretical approach is described. Results are presented and discussed in Sec. III. Finally, Sec. IV is devoted to conclusions.

II. MODEL AND METHODS

The ground state electronic structure calculations are carried out within density functional theory (DFT) by using the first-principles self-consistent method implemented in the SIESTA package.[21,22] The calculations of the conductance are done within the formalism of Green's function combined with DFT, as implemented in the TRANSIESTA software.[23] The exchange-correlation energy and electron-ion interaction are described by the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)[24] and norm-conserving pseudopotentials in the fully nonlocal form, respectively. Careful convergence studies of the conductance as a function of the basis set have shown that a double-ζ polarized (DZP) basis set is adequate,[25] especially for short molecules,[26] so we adopt a DZP basis for the Cu $4s$ orbital and the H $1s$ one, which are most involved in determining electron properties close to the Fermi level (E_F). A computationally more efficient single-ζ polarized basis set was instead used to describe the Cu $3d$ orbitals. The energy cutoff for the real-space mesh is set to 350 Ry.

We consider a junction where two Cu pyramid tips, connected to planar (111) Cu surfaces, are bridged by an H_2 molecule. Many other structures could occur in experimental conditions. However, this is one of the simplest models to be considered; it is motivated by observations of pyramidal junctions by the transmission electron microscope,[27] and it is commonly adopted for theoretical studies of quantum conductance.[8–10,13,15] We do not consider here the formation of a Cu atomic chain at the interface, since this is predicted not to occur in break junction experiments with $3d$ and $4d$ metals.[28,29] In order to describe the molecular junction we consider a periodic supercell, where the junction is oriented along the z axis. Periodicity in the xy plane is then given by a 3×3 Cu(111) cell. A slab of 10 atomic layers, with two Cu_4 pyramids placed on facing surfaces, was taken to determine optimized coordinates and energies. A scheme of the supercell is shown in Fig. 1(a). The H_2 and Cu pyramid coordinates were fully relaxed, while the coordinates of the surface layers were kept fixed to those obtained for a single tip. The junction elongation was varied by changing the distance D between the facing Cu layers of the leads. We used a 3×3 sampling of the surface Brillouin zone for structural optimizations and denser meshes, up to 15×15, when computing the transmission function.

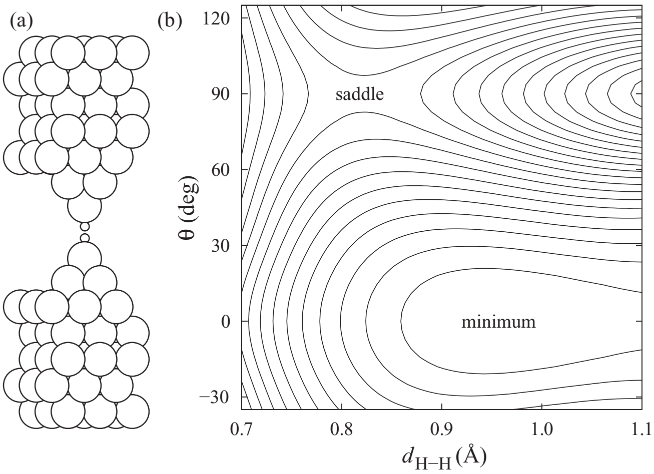

FIG. 1. (a) Scheme of the supercell adopted to represent the Cu/H_2 junction. (b) Potential energy surface of H_2 bridging two Cu tips, with $D = 11.9$ Å, as a function of the H-H distance and angle with the junction axis. Isolines are plotted every 50 meV.

III. RESULTS

We first explore the potential energy surface (PES) of the H_2 molecule embedded in the Cu junction at a fixed, intermediate distance $D = 11.9$ Å, taken here as a reference system, reported in Fig. 1(b). The molecule is placed in the midpoint between the two tips. The PES is calculated as a function of $d_{\text{H-H}}$, the interatomic distance of H_2, and θ, that is the angle between the H_2 axis and the junction axis. We see that there is one well defined energy minimum corresponding to the coaxial geometry, where $d_{\text{H-H}} = 0.95$ Å, significantly larger than the bond length in the gas phase as already pointed out for electrodes of other elements.[10] The presence of only one energy minimum tends to exclude that the low-conductance peak in the conductance histogram[20] may be due to molecules trapped in a secondary energy minimum. We notice that, by relaxing the H_2 molecule in the presence of biases up to $V = 0.5$ eV (a value higher than the usual voltages applied in the experiment), we did not observe changes in the PES described above. This can exclude that a transition to a secondary minimum, absent at zero bias, may appear with an applied voltage.

The projected density of states (PDOS) onto the orbitals of the H species and of the apical Cu atoms is shown in Fig. 2(a) for this reference system ($D = 11.9$ Å) at the PES minimum. The bonding state of H_2 yields a well defined peak near -8 eV (well below the $4d$ band of Cu), while the antibonding state results strongly hybridized with the $4s$ band of Cu, giving rise to a shallow contribution around E_F. Accordingly the transmission function $T(E)$, which at E_F assumes the value of 0.8, remains almost flat for a wide range around that energy,

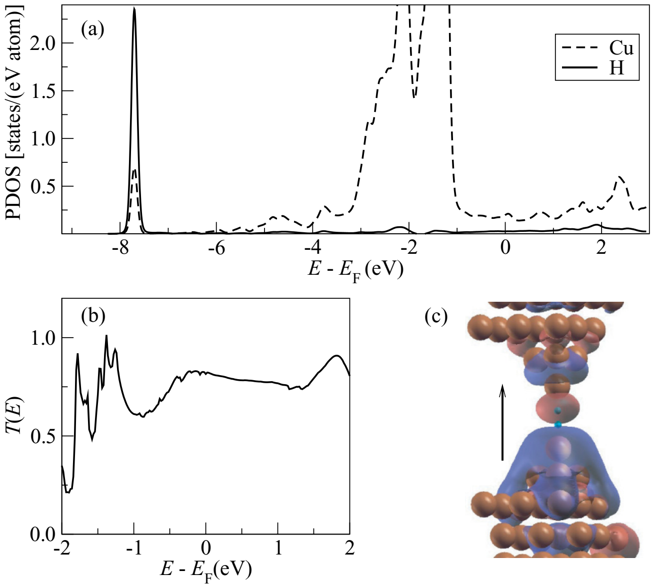

FIG. 2. (Color online) (a) PDOS on the H and apical Cu atoms and (b) transmission function of H_2 bridging two Cu electrodes with $D = 11.9$ Å. (c) Eigenvector of the most transmitting eigenchannel, in the direction indicated by the arrow, calculated at $\bar{\Gamma}$.

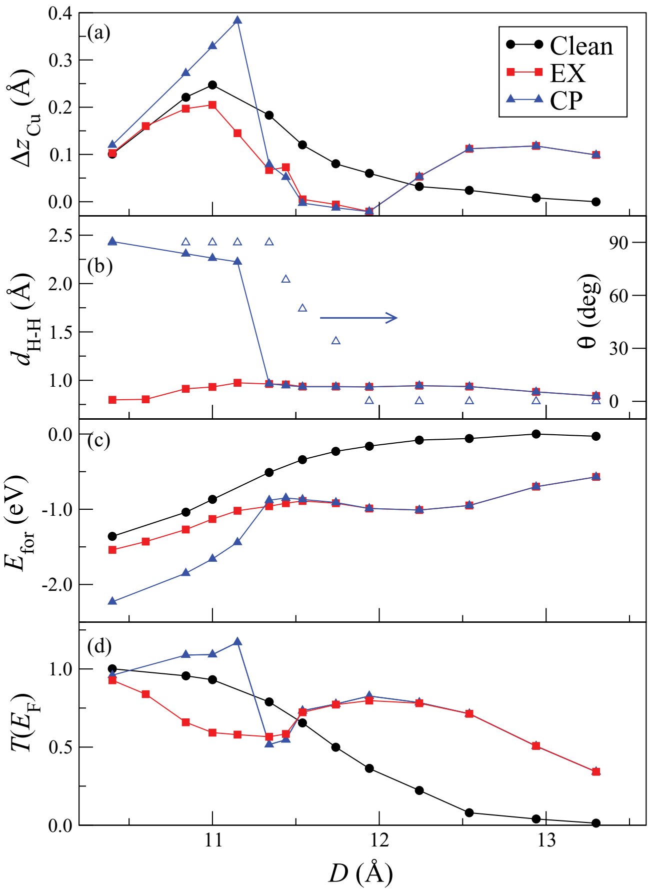

FIG. 3. (Color online) Cu/H_2/Cu junctions. The graph reports (a) the apical Cu displacement Δz_{Cu} with respect to the isolated lead, (b) the H-H interatomic distance $d_{H\text{-}H}$ along with the H_2 torsion angle θ, (c) the junction formation energy, and (d) transmission function at the Fermi level $T(E_F)$ as a function of the electrode separation D. Results are shown for the case of clean junction (black circles) and of H_2 junctions during expansion (EX, red squares) and compression (CP, blue triangles).

while it shows features below −1 eV in correspondence to the onset of the Cu d band, see Fig. 2(b). A calculation of the eigenchannels[30] of this system reveals that only one channel is open at $\bar{\Gamma}$, contributing to 95% of the total conductance. Its eigenvector is illustrated in Fig. 2(c). Our calculations show that, for this value of D, the transmission function is largest when the molecule is oriented along the junction axis. In fact, for angles θ equal to 0°, 45°, and 90° the transmission function evaluated at E_F amounts to 0.8, 0.7, and 0.4, respectively.

Next, we discuss the structural and conductive properties of the junction as the electrode separation increases by an external mechanical manipulation, starting from a Cu-Cu point contact configuration. For any given distance D, we relaxed the structure and computed the transmission function. In Fig. 3 the main results are summarized and will be discussed in the following. Namely, we show (a) the displacement height difference Δz_{Cu} of the Cu atom at the pyramid apex with respect to that of a single Cu_4 pyramid, (b) the H-H interatomic distance $d_{H\text{-}H}$ along with its torsion angle θ, (c) the junction formation energy with reference to the two leads and H_2 molecule, and (d) the transmission function at the Fermi level $T(E_F)$ as a function of the electrode separation D. We start by considering the case of a clean junction. The shortest value of D we consider (≈10.4 Å) corresponds to a distance between the Cu apical atoms of 2.42 Å, slightly shorter than the one in bulk Cu. The conductance approaches unity as expected for s-metal point contacts, see Fig. 3(d). In fact, in such conditions the number of open conducting channels is determined by the valence orbitals of the contacting atoms relevant at E_F.[31] As the distance between the electrodes increases, the Cu tips are pulled outwards by as much as 0.25 Å, see Fig. 3(a), while the conductance decreases. By looking to the formation energy [Fig. 3(c)] and $T(E_F)$ [Fig. 3(d)] we can consider the bond between the two Cu apical atoms as broken for D larger than about 12.5 Å. Beyond that distance the transmission decays exponentially, showing a tunneling regime.

When taking into account H_2, we consider both the case of a molecule that is approaching the junction during its elongation, as well as one in which it is trapped between the electrodes during compression. To this purpose, D was varied following two different paths, which we denote as expansion (EX) and compression (CP) and are depicted in Fig. 4: In the EX case H_2 was placed at the side of the tips contact, ending with the molecule fitting inside the tip gap at large D; this configuration is then the starting point for the CP case, where D is progressively reduced. We focus first on the EX case. For short electrode separations the H_2 binds molecularly next to the junction (see Fig. 4, upper panel) without affecting significantly its structure. We also notice that $d_{H\text{-}H}$ assumes its lowest value, close to the gas-phase one, see Fig. 3(b). As long as H_2 remains outside the gap ($D < 11.5$ Å) it acts as a perturbation to the transmission, which is lower than that of the clean junction. In fact, one can see that $T(E_F)$ reaches a minimum of about 0.56 [Fig. 3(d)]. As D increases the

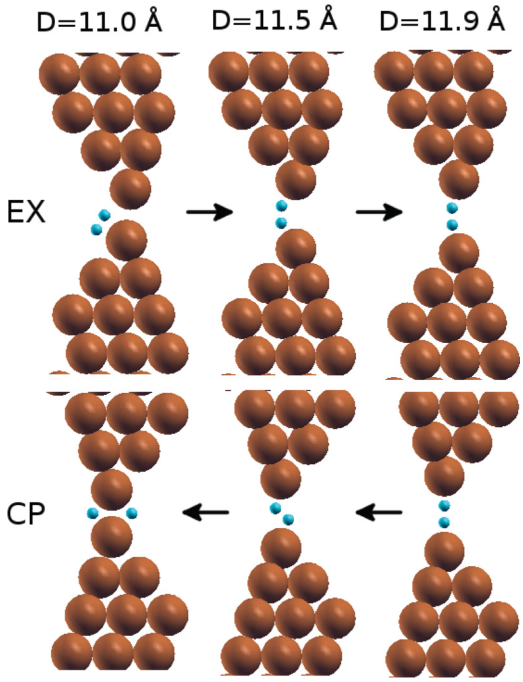

FIG. 4. (Color online) Relaxed configuration of Cu-Cu junction with adsorbed H_2 for three different distances D; both EX and CP geometries are shown.

molecule progressively approaches the gap and, at $D = 11.4$ Å the distance between the apical Cu atoms is large enough to accommodate the molecule in the gap. From this distance on, the transmission is considerably higher in the presence of H_2, and it remains almost constant to a value of 0.8 for 11.5 Å $< D < 12.5$ Å. It is interesting to note that, as long as $D < 12.5$ Å, H_2 pushes the tips away from each other, with a Cu-Cu distance larger than in the clean case [Fig. 3(a)]. Conversely, for $D > 12.5$ Å it pulls the tips closer by about 0.2 Å.

We discuss now the CP stage. By shrinking the junction to approximately $D \approx 11.5$ Å, the properties are identical to the EX stage. The situation becomes more interesting as D is further decreased. We notice that the molecule progressively tilts [see the trend of θ in Fig. 3(b)] with its axis rotating from the axial direction ($\theta = 0$) to an orthogonal one ($\theta = 90°$). Eventually, by reducing D the molecular dissociation is favored and the two H atoms lie far from each other on two different sides of the junction (Fig. 4, lower panel): One obtains $d_{\text{H-H}} > 2$ Å for $D < 11.4$ Å. This also stabilizes the contact and makes the apex Cu atoms move outwards and approach each other, see Fig. 3(a), with significant enhancement of conductance with respect both to clean and EX cases. It is remarkable that at all stages of the CP path, the energy of the system, reported in Fig. 3(c), is no higher than in the corresponding EX case, showing that the molecule is favored to remain inside the gap during compression and especially that dissociated adsorption is stabilized. We stress that dissociation does not occur spontaneously during the initial elongation as a result of some energy barrier (not determined here).

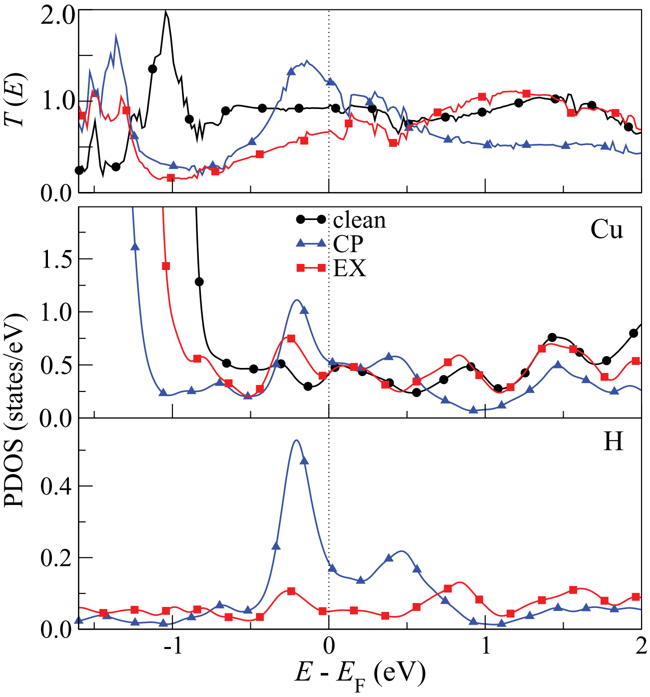

FIG. 5. (Color online) Cu/H_2/Cu junction for $D = 11.0$ Å. Transmission functions (upper panel) and PDOS on H and on the apical Cu atoms (lower panels) for the Cu/H_2/Cu junction with $D = 11.0$ Å in the clean (black dots), CP (blue triangles), and EX (red squares) configurations.

To inspect the origin of the differences in the transmission functions especially at low D, in Fig. 5 we show the DOS, the PDOS, and the transmission functions for the three different structures considered with $D = 11.0$ Å, namely the clean junction, the one with dissociated hydrogen atoms (CP), and that with H_2 in an asymmetric position (EX). By comparing the two PDOS on H one can notice a stronger contribution near E_F for CP, which results in a higher $T(E_F)$ with respect to the clean case. Furthermore, we recall that the Cu apex atoms are closest in the presence of dissociated H_2. On the other side, for EX the PDOS around E_F is very broad following the hybridization of the molecular LUMO with the Cu tips. Accordingly, we notice that the $T(E_F)$ has a lower value than in the other two cases. In the case of the dissociated molecule, we found that two eigenchannels are open, one with even symmetry with respect to the plane normal to the H-H axis and the other with odd symmetry, accounting for 0.58% and 0.42% of the conductance at $\bar{\Gamma}$, respectively.

From our calculations one can deduce a qualitative trend for the conduction in the presence of H_2. While for the clean configuration the conductance is close to 1 G_0 and tends rapidly to zero as the point contact is broken, in the presence of H_2 we have a more complex situation. The conductance varies from 0.5 G_0 to 1.0 G_0 and spans values in this range even for large electrode separations, at which it would be suppressed in the absence of the molecule. We found that the lowest conductive configurations are those in which the H_2 is not coaxial with the junction axis and sits laterally on one side of the contact. Thus, our results suggest that the low conductance peak found by Kiguchi and coworkers may not be the signature of the formation of a single molecular junction, but rather that it may be attributed to configurations where the molecule is not centered in the junction. Of course, in such cases the H_2 coupling to the two electrodes is asymmetric, which implies a reduction of the overall conductance.[20] The discrepancy we found from the experimental ≈ 0.2 G_0 value of low conductance can have several origins. It can be due to the intrinsic limitations of ground-state DFT applied to electronic transport, to the self-interaction error,[20,32,33] or to too simplistic models of the junction geometry. For distances at which the coaxial geometry is favored ($D > 11.7$ Å), the conductance restores the ≈ 1 G_0 value. Accordingly, we point out that the 1 G_0 peak in the measured conductance histogram may not only involve Cu point contacts, but also molecular junctions with the H_2 axis parallel to the transport direction and those with dissociated molecules. In addition, this interpretation can also account for the broadening and shift in energy of the main peak that one may appreciate in the conductance histogram.[20] In fact, the conductance values for coaxial configurations ($D > 11.5$ Å) are lower and more distributed than those of the clean contacted junction ($D < 11.0$ Å). We finally note that in our view the experimental instability of the low conductance junctions could be justified as a consequence of the migration of a laterally adsorbed molecule far from the contact region, as well as to its dissociation.

The ballistic regime of the electron transport cannot be sustained if the conducting electrons can transfer their kinetic energy to the vibrational modes of the junctions. Additionally, a comparison between the measured inelastic electron tunneling spectroscopy (IETS) active frequencies and calculated

TABLE I. Vibrational modes of H_2 bridging two Cu tips, with $D = 11.9$ Å. Gas phase experiments from Ref. 34.

Mode	Frequency (cm^{-1})
ω_1	399
ω_2	511
ω_3	1313
ω_4	2178
Gas phase	4132
Experiments	4160

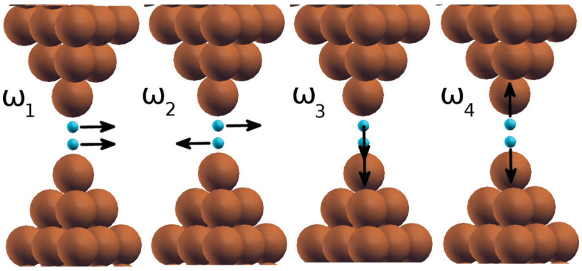

FIG. 6. (Color online) Displacement eigenvectors of the vibrational modes of H_2 bridging two Cu tips, with $D = 11.9$ Å.

ones could provide a hint on the contact geometry. In particular, the Cu/H_2/Cu junction exhibits a 1 G_0 peak in conductance traces which was attributed to Cu atomic contacts,[20] but which our results suggest to be consistent with coaxial molecular junctions as well. To provide additional insight in the properties of the junction, and to check this possibility by comparing with future IETS measurements in the high conductance regime, we compute the dynamical properties of the molecular H_2-bridged contact in the coaxial configuration at a representative distance [$D = 11.9$ Å, see Fig. 1(a)]. Our calculated value for the vibrational energy of the hydrogen molecule in the gas phase is in good agreement with the experimental findings,[34] as can be observed in Table I, where the vibrational frequencies of the molecule in the junction are also collected. We take into account the H degrees of freedom only. One has a shuttle mode (center of mass oscillation) in the xy plane with frequency ω_1, a wobble mode (fixed center of mass, rotation of the molecular axis) with frequency ω_2, a shuttle mode along the z direction with frequency ω_3, and a stretching mode (variation of the H-H interatomic distance) with frequency ω_4. The eigendisplacements are depicted in Fig. 6. In particular, notice the lowest-energy shuttle mode, with a frequency amounting to $\omega_1 = 399\ cm^{-1}$ (49 meV) at the contact distance considered. IETS measurements of molecular Cu/H_2/Cu junctions in the high conductance regime could be desirable.

Deeper vibrational analysis, both theoretical and experimental, beside interpreting available IETS data in the very low conductance regime, could further allow one to address the dependence of the junction properties with bias, already pointed out by the disappearance of the low-conductance 0.2 G_0 peak with increasing voltage.[20]

IV. CONCLUSIONS

We have performed first-principles calculations to shed light on the structural and conductive behavior of Cu/H_2/Cu junctions, showing the most probable geometries at each interelectrode distance with the aim to give a general trend of the junction properties upon its elongation and compression. At short distances between the electrodes, H_2 molecules can adsorb at the side of the junction, and are eventually trapped inside as the distance is increased. Following compression yields to molecular dissociation without any energy barrier. This results in the increase of the transmission function at the Fermi level, with respect to the lateral molecule at the same tip-tip distance, which can be connected to a larger density of states in the junction region and to closer metal atoms. The low conductance value found experimentally has been tentatively attributed to asymmetric junctions at low tip distances, in which the H_2 bond at the side of the junction causes a disturbance to the electronic conductance. A high conductance state with symmetric configuration at larger distances could be degenerate with that of clean contacts. This effect could be disentangled by comparison of IETS measurements with calculated vibrational modes, which we provide for a coaxial Cu/H_2/Cu junction.

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