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Published in:
Physical Review B Condensed Matter

Link to article, DOI:
[10.1103/PhysRevB.71.161402](https://doi.org/10.1103/PhysRevB.71.161402)

Publication date:
2005

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Djukic, D., Thygesen, K. S., Untiedt, C., Smit, R. H. M., Jacobsen, K. W., & Ruitenbeek, J. M. V. (2005). Stretching dependence of the vibration modes of a single-molecule Pt-H-2-Pt bridge. *Physical Review B Condensed Matter*, 71(16), 161402. <https://doi.org/10.1103/PhysRevB.71.161402>

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Stretching dependence of the vibration modes of a single-molecule Pt-H₂-Pt bridge

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(Received 19 January 2005; published 20 April 2005)

A conducting bridge of a single hydrogen molecule between Pt electrodes is formed in a break junction experiment. It has a conductance near the quantum unit, $G_0=2e^2/h$, carried by a single channel. Using point-contact spectroscopy three vibration modes are observed and their variation upon isotope substitution is obtained. The stretching dependence for each of the modes allows uniquely classifying them as longitudinal or transversal modes. The interpretation of the experiment in terms of a Pt-H₂-Pt bridge is verified by density-functional theory calculations for the stability, vibrational modes, and conductance of the structure.

DOI: 10.1103/PhysRevB.71.161402

PACS number(s): 73.63.Rt, 63.22.+m, 73.23.-b, 85.65.+h

There is beauty and power in the idea of constructing electronic devices using individual organic molecules as active elements. Although the concept was proposed as early as 1974 (Ref. 1) only recently are experiments aimed at contacting individual organic molecules being reported^{2–11} and devices being tested.^{12,13} The first results raised high expectations, but quickly problems showed up, including as large discrepancies between the current-voltage characteristics obtained by different experimental groups, and large discrepancies between experiments and theory. The main tools that have been applied in contacting single molecules are scanning tunneling microscope (or conducting tip atomic force microscope) and break junction devices. Often it is difficult to show that the characteristics are due to the presence of a molecule, or that only a single molecule has been contacted. There has been important progress in analysis and reproducibility of some experiments,^{4,5,8–11} but in comparing the data with theory many uncertainties remain regarding the configuration of the organic molecule and the nature of the molecule-metal interface. The organic molecules selected for these studies are usually composed of several carbonyl rings and are anchored to gold metal leads by sulphur groups. In view of the difficulties connected with these larger molecules it seems natural to step back and focus on even simpler systems.

Here we concentrate on the simplest molecule, H₂, anchored between platinum metal leads using mechanically controllable break junctions. Experiments on this system¹⁴ showed that the conductance of a single hydrogen molecule between Pt leads is slightly below $1G_0$, where $G_0=2e^2/h$ is the conductance quantum. A vibration mode near 65 meV was observed and interpreted as the longitudinal center-of-mass (CM) mode of the molecule. These results have inspired further calculations on this problem using density-functional theory (DFT) methods.^{15,16} Cuevas *et al.*¹⁵ find a conductance around $0.9G_0$, in agreement with the DFT calculations presented in Ref. 14. In contrast, García *et al.*¹⁶ obtain a conductance of only $(0.2–0.5)G_0$ for the in-line configuration of the hydrogen molecule. Instead, they propose an alternative configuration with hydrogen atoms sitting above and below a Pt—Pt atomic contact.

In this Communication we combine experimental results with DFT calculations to show that the configuration proposed in Ref. 14 is correct, yet the observed vibration mode was incorrectly attributed. In contrast, the present experiment resolves three vibration modes that can be classified as longitudinal or transverse modes based on the observed shifts with stretching of the contacts. The comparison with the calculations is nearly quantitative and the large number of experimentally observed parameters (the number of vibration modes, their stretching dependence and isotope shifts, the conductance and the number of conductance channels) puts stringent constraints on any possible interpretation.

The measurements have been performed using the mechanically controllable break junction technique.^{17,18} A small notch is cut at the middle of a Pt wire to fix the breaking point. The wires used are 100 μm in diameter, about 1 cm long, and have a purity of 99.999 99%. The wire is glued on top of a bending beam and mounted in a three-point bending configuration inside a vacuum chamber. Once under vacuum and cooled to 4.2 K the wire is broken by mechanical bending of the substrate. Clean fracture surfaces are exposed and remain clean for days in the cryogenic vacuum. The bending can be relaxed to form atomic-sized contacts between the wire ends using a piezoelement for fine adjustment.

After admitting a small amount ($\sim 3 \mu\text{mol}$) of molecular H₂ (99.999%) in the sample chamber and waiting some time for the gas to diffuse to the cold end of the insert, a sudden change is observed in the conductance of the last contact before breaking. The typical value of $(1.6\pm 0.4)G_0$ for a single-atom Pt contact is replaced by a frequently observed plateau near $1G_0$ that has been attributed in Ref. 14 to the formation of a Pt-H₂-Pt bridge. By increasing the bias voltage above 300 mV we recover the pure Pt conductance. But as soon as the bias voltage is decreased the H₂-induced plateaus at $1G_0$ reappear. We interpret this as desorption of hydrogen due to joule heating of the contacts. For biases below 100 mV, the Pt-H₂-Pt bridge can be stable for hours.

At the $1G_0$ -conductance plateaus we take differential conductance (dI/dV) spectra in order to determine the inelastic scattering energies. By repeatedly breaking the contacts, joining them again to a large contact, and pulling until

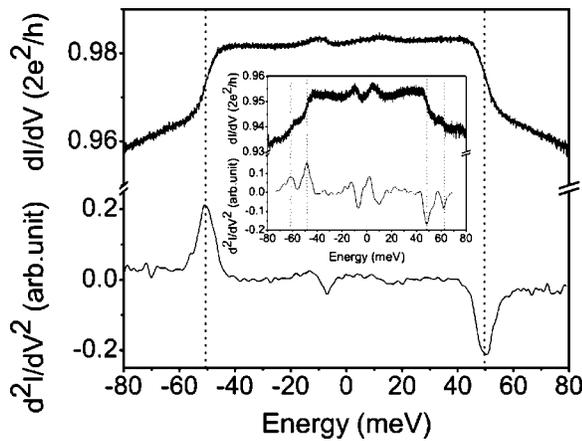


FIG. 1. Differential conductance curve for D_2 contacted by Pt leads. The dI/dV curve (top) was recorded over 1 min, using a standard lock-in technique with a voltage bias modulation of 1 meV at a frequency of 700 Hz. The lower curve shows the numerically obtained derivative. The spectrum for H_2 in the inset shows two phonon energies, at 48 and 62 meV. All spectra show some, usually weak, anomalies near zero bias that can be partly due to excitation of modes in the Pt leads, partly due to two-level systems near the contact (Ref. 19).

arriving at a plateau near $1G_0$, we obtain a large data set for many independent contacts. The experiments were repeated for more than five independent experimental runs, and for the isotopes HD (96%) and D_2 (99.7%). Figure 1 displays a spectrum taken for D_2 showing a sharp drop in the differential conductance by 1%–2% symmetrically at ± 50 meV. Such signals are characteristic for point-contact spectroscopy,²⁰ which was first applied to single-atom contacts in Ref. 21. The principle of this spectroscopy is simple: when the difference in chemical potential between left- and right-moving electrons, eV, exceeds the energy of a vibration mode, $\hbar\omega$, backscattering associated with the emission of a vibration becomes possible, giving rise to a drop in the conductance. This can be seen as a dip (peak) in the second derivative d^2I/dV^2 at positive (negative) voltages, as in Fig. 1.

Some contacts can be stretched over a considerable distance, in which case we observe an *increase* of the vibration mode energy with stretching. This observation suffices to invalidate the original interpretation¹⁴ of this mode as the longitudinal CM mode. Indeed, our DFT calculations show that the stretching mainly affects the Pt-H bond which is elongated and weakened resulting in a drop in the frequency of the H_2 longitudinal CM mode. An increase can be obtained only for a transverse mode which, like a guitar string, obtains a higher pitch at higher string tension due to the increased restoring force.

On many occasions we observe two modes in the dI/dV spectra, (see the inset of Fig. 1). The relative amplitude of the two modes varies: some spectra show only the lower mode, some only the higher one. All frequencies observed in a large number of experiments are collected in the histograms shown in Fig. 2. With a much larger data set compared to Ref. 14 we are now able to resolve two peaks in the

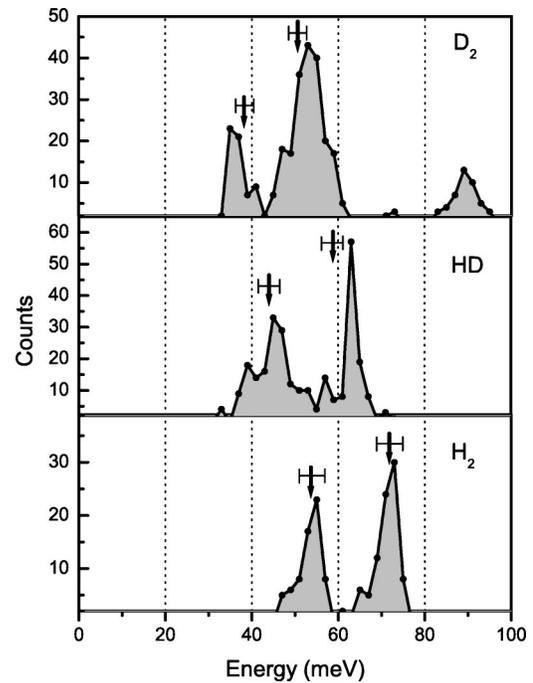


FIG. 2. Distribution of vibration mode energies observed for H_2 , HD, and D_2 between Pt electrodes, with a bin size of 2 meV. The peaks in the distribution for H_2 are marked by arrows and their widths by error margins. These positions and widths were scaled by the expected isotope shifts, $\sqrt{2/3}$ for HD and $\sqrt{1/2}$ for D_2 , from which the arrows and margins in the upper two panels have been obtained.

distribution for H_2 corresponding to the two modes seen in the inset of Fig. 1. The peaks are expected to shift with the mass m of the isotopes as $\omega \propto \sqrt{1/m}$. This agrees with the observations, as shown by the scaled position of the hydrogen peaks marked by arrows above the distributions for D_2 and HD. Note that the distribution for HD proves that the vibration modes belong to a molecule and not to an atom, since the latter would have produced a mixture of the H_2 and D_2 distributions. In the case of D_2 we observe a third peak in the distribution at 86–92 meV. For the other isotopes this mode falls outside our experimentally accessible window of about ± 100 meV, above which the contacts are destabilized by the large current. Figure 3 shows the dependence of this mode upon stretching of the junction. In contrast to the two low-frequency modes this mode shifts down with stretching, suggesting that this could be the longitudinal CM mode that was previously attributed to the low-frequency modes.¹⁴

In order to test the interpretation of the experiment in terms of a Pt- H_2 -Pt bridge we have performed extensive DFT calculations using the plane-wave-based pseudopotential code DACAPO.^{22,23} The molecular contact is described in a supercell containing the hydrogen atoms and two 4-atom Pt pyramids attached to a Pt(111) slab containing four atomic layers (see inset of Fig. 4, Ref. 24). In the total-energy calculations both the hydrogen atoms and the Pt pyramids were relaxed while the remaining Pt atoms were held fixed in the bulk structure. The vibration frequencies were obtained by diagonalizing the Hessian matrix for the two hydrogen atoms. The Hessian matrix is defined by $\partial^2 E_0 / (\partial \tilde{u}_{n\alpha} \partial \tilde{u}_{m\beta})$,

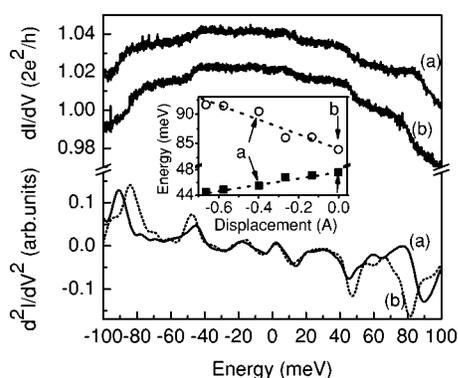


FIG. 3. dI/dV spectrum (top) for Pt- D_2 junctions and their numerical derivatives d^2I/dV^2 (bottom). The spectrum (b) was obtained on the same contact as (a) after stretching the junction by 0.04 nm. They are two spectra out of a series of six and the complete evolution of the two modes is shown in the inset.

where E_0 is the ground-state potential-energy surface and $\tilde{u}_{n\alpha}$ is the displacement of atom n in direction α multiplied by the mass factor $\sqrt{M_n}$. In calculating the vibration modes all Pt atoms were kept fixed, which is justified by the large difference in mass between H and Pt. The conductance is calculated from the Meir-Wingreen formula²⁷ using a basis of partly occupied Wannier functions,²⁸ representing the leads as bulk Pt crystals.

In order to simulate the stretching process of the experiment we have calculated contacts for various lengths of the supercell. The bridge configuration is stable over a large distance range with the binding energy of the H_2 molecule varying from -0.92 to -0.47 eV, relative to gas phase H_2 and a broken Pt contact, over the range of stretching considered here. The H-H bond length stays close to 1.0 Å during the first stages of the stretching upon which it retracts and approaches the value of the free molecule. The hydrogen thus retains its molecular form and the elongation mainly affects the weaker Pt-H bond. For smaller electrode separations a structure with two hydrogen atoms adsorbed on the side of a Pt-Pt atomic contact becomes the preferred geometry, as also found by García *et al.*¹⁶ However, we find that the latter structure has a conductance of $1.5G_0$, well above $1G_0$. Moreover, this structure has at least three conduction channels with significant transmission, which excludes it as a candidate structure based on the analysis of conductance fluctuations in Refs. 14 and 29, which find a single channel only. In view of the activity of the Pt surface towards catalyzing hydrogen dissociation one would have anticipated a preference for junctions of hydrogen in atomic form. However, we find that the bonding energy of H compared to that of H_2 strongly depends on the metal coordination number of the Pt atom. For metal coordination numbers smaller than 7, bonding to molecular hydrogen is favored, the bond being strongest for fivefold-coordinated Pt.

The calculations identify the six vibrational modes of the hydrogen molecule. For moderate stretching, two pairwise-degenerate modes are lowest in frequency. The lowest one corresponds to translation of the molecule transverse to the transport direction while the other one is a hindered rotation

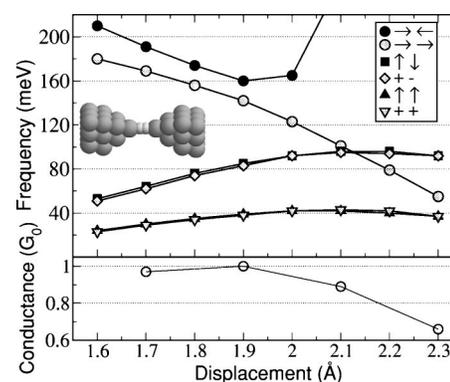


FIG. 4. Calculated vibrational frequencies for the hydrogen atoms in the contact as a function of elongation of the supercell. The inset shows the atomic arrangement in the supercell. The lower panel shows the calculated conductance.

mode. The two modes are characterized by increasing frequencies as a function of stretch of the contact. At higher energies we find the two longitudinal modes: first the CM mode and then the internal vibration of the molecule. These two modes become softer during stretching up to Pt-H bond lengths of about 1.9 Å. Beyond this point the Pt-H bond begins to break and the internal vibration mode approaches the one of the free molecule.

The variation of the frequencies of the lowest-lying hydrogen modes with stretching is thus in qualitative agreement with the experiments, a strong indication that the suggested structure is indeed correct. The agreement is even semiquantitative: If we focus on displacements in the range 1.7–2.0 Å (see Fig. 4) the calculated conductance does not deviate significantly from the experimentally determined value close to $1G_0$. In this regime the three lowest calculated frequencies are in the range 30–42, 64–92, and 123–169 meV. The two lowest modes can be directly compared with the experimentally determined peaks at 54 and 72 meV observed for H_2 , while a mass rescaling of the D_2 result for the highest mode gives approximately 126 meV.

The second peak in the HD distribution in Fig. 2 is somewhat above the position obtained by scaling the H_2 peak by $\sqrt{3/2}$. The transverse translation mode and the hindered rotation mode are decoupled when the two atoms of the molecule have the same mass. In the case of HD they couple and the simple factor does not hold. Having identified the character of these modes a proper rescaling of the experimentally determined H_2 frequencies (54 and 72 meV) to the case of HD leads to the frequencies 42 and 66 meV, in very good agreement with the peaks observed for HD.

Even though there is good agreement with the calculated signs of the frequency shifts with stretching for the various modes, there is a clear discrepancy in magnitudes. Considering, e.g., the high-lying mode for D_2 , the measured shift of the mode is of the order 15 meV/Å, which is almost an order of magnitude smaller than the calculated variation of around 130 meV/Å. However, experimentally the distances are controlled quite far from the molecular junction and the elastic response of the electrode regions have to be taken into account. Simulations of atomic chain formation in gold³⁰ dur-

ing contact breaking show that most of the deformation happens not in the atomic chains but in the nearby electrodes. A similar effect for the Pt-H₂-Pt system will significantly reduce the stretch of the molecular bridge compared to the displacement of the macroscopic electrodes.

The observation of the three vibration modes and their stretching dependence provides a solid basis for the interpretation. The fourth mode, the internal vibration, could possibly be observed using the isotope tritium. The hydrogen molecule junction can serve as a benchmark system for molecular electronics calculations. The experiments should

be gradually expanded towards more complicated systems and we have already obtained preliminary results for CO and C₂H₂ between Pt leads.

We thank M. Suty for assistance in the experiments and M. van Hemert for many informative discussions. This work was supported by the Dutch “Stichting FOM,” the Danish Center for Scientific Computing through Grant No. HDW-1101-05, the Spanish MCyT under Contract No. MAT-2003-08109-C02-01 and the Ramón y Cajal program, and the ESF through the EUROCORES SONS programme.

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