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Excitation of Jahn−Teller Active Modes during Electron Transport through Single C_{60} Molecules on Metal Surfaces

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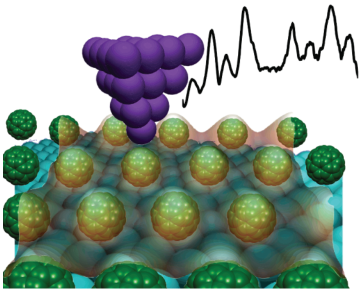
ABSTRACT Using scanning tunneling spectroscopy, we resolve all Jahn−Teller active H_g modes of a single C_{60} molecule when adsorbed on a Pb(111) surface. Selection rules for vibrational excitation in inelastic tunneling spectra are thus given by the electron−phonon coupling in the molecular orbital close to the Fermi level. The observation of modes depends, however, crucially on the orbital alignment. In particular, inelastic spectra in a resonant tunneling regime, as realized by adsorption of C_{60} on Cu(111), show no vibrational fingerprint.

SECTION Electron Transport, Optical and Electronic Devices, Hard Matter



Inelastic electron tunneling spectroscopy (IETS) has become an essential tool for the understanding of a large variety of phenomena at the single-molecule scale, such as chemical reactions,[1,2] molecular luminescence,[3,4] magnetism,[5,6] current-induced heating,[7,8] and so forth. IETS is not exclusively connected to the excitation of molecular vibrations in the tunneling regime;[9] similar inelastic processes are also present in electronic transport through molecules in contact with both electrodes.[10] Consequently, the search of an intuitive set of basic rules that explain and predict inelastic effects has been a priority during the past years.[11]

IETS is essentially defined as a nonresonant tunneling process, in which the excitation of a vibrational mode connects two states separated by the mode eigenenergy. The first theoretical models of IETS determined that the mode excitation is more effective when the transient population of an adsorbate (or adsorbate-induced) resonance is involved.[12−14] This model entails a set of excitation selection rules based on the symmetry of the one-electron state and the induced molecular distortions. It also predicts that the proximity of a molecular resonance to the Fermi level (E_F) should enhance the inelastic signal. Such clear predictions, however, have not been experimentally demonstrated: IETS usually resolves a very few number of modes; in fact, for many substrate/molecule systems, it resolves none at all. From a large variety of experimental results and theoretical simulations, the rules selecting which vibrations effectively play a role in IETS are found to be more diffuse than expected and are rather defined as propensity rules.[15] These rules can explain the vibrational activity of small chemisorbed adsorbates,[16,17] where contributions from many orbitals mix at the Fermi level, and of systems with poor density of molecular states at the Fermi level, such as saturated hydrocarbons.[18] It is rare to find adsorption systems with a fairly unperturbed molecular state close to E_F, where one could test the full validity of an excitation model mediated by molecular resonances.

A well-suited candidate to study the vibrational selection rules in such a system is the fullerene C_{60} molecule, because its 46 vibrational states are distributed in 10 different point group symmetries. Among these, one set of modes shows enhanced Jahn−Teller (JT) type of electron−phonon (*e*−*ph*) coupling, which arises from the high degeneracy of the electronic levels.[19] Excitation of the JT active modes of C_{60} has been observed in photoemission,[20] electroluminiscence,[4] and resonant transport experiments[21−23] when the molecules weakly interact with the substrate. However, surprisingly, fullerenes on a metal surface show a very weak vibrational activity when investigated with IETS,[23−27] contrasting with the theoretical predictions stating that the whole set of JT modes should be excited.[28]

In this letter, we report the observation of the complete set of JT active modes in the IET spectra of single C_{60} molecules adsorbed on Pb(111), which appears to be absent when C_{60} lies on other surfaces, such as those of noble metals. We show that the proximity of the lowest unoccupied molecular orbital (LUMO) with respect to the substrate Fermi level (E_F) enhances the detection of molecular vibrations in the scanning tunneling microscope (STM) junction. This fact is an experimental confirmation of the resonant model of vibrational excitation introduced by Persson and Baratoff.[12] However, when the resonance is centered at the Fermi level, the IETS signal vanishes completely, suggesting that other factors such as fast vibrational damping may also play a role.

On Pb(111), Ag(110), and Cu(111), as on many other metal surfaces, C_{60} molecules form hexagonal arrangements with a close-packed distance of ∼10 Å [inset of Figure 1a for C_{60} on Pb(111)]. C_{60} molecules embedded in such islands are very stable, allowing us to inspect their transport properties in a broad range of junction conductances. This can be achieved by approaching the STM tip a distance z_{appr} toward a single C_{60} molecule at constant sample bias.[7,8] For C_{60} on Pb(111), the tunnel regime (identified as the exponential regime in the

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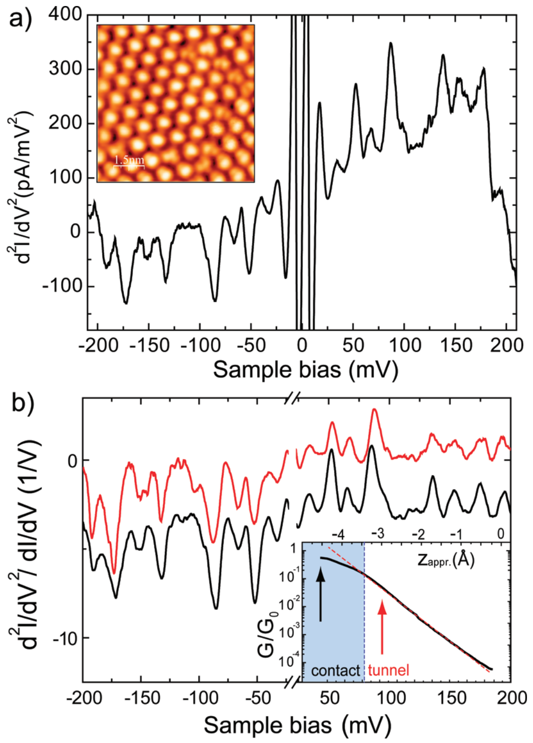

Figure 1. (a) Inelastic tunneling spectrum of a C_{60} molecule embedded in a hexagonal island (inset) on Pb(111).[38] The spectrum (and all others in this paper) is recorded as the second harmonic signal by the lock-in technique (f_{mod} = 723 Hz, U_{mod} = 6 mV_{rms}). Here, the tip is moved 5 Å toward the molecule, where a mechanical contact between the tip and fullerene is formed. The broad background is associated with the curvature of the onset of the LUMO derived resonance. The oscillations around the Fermi level are due to the superconducting gap of the tip and substrate and can be equally found in spectra on the bare Pb surface. (b) d^2I/dV^2 spectra at two different tip−molecule distances representing the tunnel and contact regime. The d^2I/dV^2 spectra are normalized by their differential conductance dI/dV for their comparison. (Inset) Increase of the junction conductance G as the tip is moved from a distance z_{appr} toward a C_{60} molecule (U_b = 400 mV, and I_t = 1.2 nA initially). The arrows mark the points where the IETS spectra were measured.

$I - z_{appr}$) extends until the junction conductivity reaches $\sim 0.1 G_0$ (G_0: quantum of conductance). Beyond this point, the current smoothly levels off to a flatter $I - z_{appr}$ behavior, the region of the mechanical tip−C_{60} contact. A typical inelastic spectrum ($d^2I/dV^2 - V$) of a single C_{60} molecule on Pb(111) is shown in Figure 1a in the contact regime. We can identify nine peaks at positive sample bias and nine dips at the corresponding negative bias voltages on top of a broad background. Each peak−dip pair marks the excitation threshold for a molecular vibration by reflecting its corresponding increase in junction's conductance.

The observation of this vibrational fingerprint is robust, being observed with the same shape in the tunnel and contact regimes. Figure 1b shows a comparison between two consecutive spectra taken after moving the STM tip 3 Å and 4.5 Å toward the fullerene, hence for junction conductances of 0.03 G_0 and 0.25 G_0, representing the tunnel and contact regimes, respectively. Both spectra, normalized by their differential conductance, show the same vibrational modes with similar intensity and line shape. Mechanically controlled break junction experiments found a transition from peaks to dips in the inelastic spectra when going from tunnel to contact regime.[29] The origin of this was attributed to enhanced inelastic transitions into backscattering states in contact, with the crossover between the two regimes being defined by a conductance of 0.5 G_0 per transmission channel.[17] Thus, the low contact conductance found for C_{60} on Pb(111) causes this system to still behave as a tunnel junction.

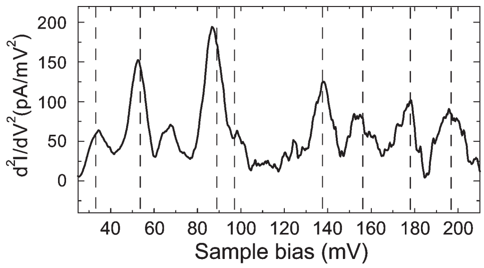

Figure 2. d^2I/dV^2 spectrum of Figure 1a, after background subtraction, zoomed at positive sample bias. The dashed lines indicate the energies of the eight H_g modes of a free C_{60} molecule.[39]

Table 1. Table of Vibrational Modes Detected in the IETS Spectra with Their Symmetry and Change of Conductance

$\hbar\omega_\nu$ (meV)	mode (ν)	$\Delta G/G$ (%)
34 ± 2	$H_g(1)$	1.4
52 ± 2	$H_g(2)$	5.2
67 ± 2	$A_g(1)$ or $T_{1u}(1)$	2.2
87 ± 2	$H_g(3)$	5.6
97 ± 3	$H_g(4)$	1.6
137 ± 2	$H_g(5)$	3.5
155 ± 2	$H_g(6)$	2.1
175 ± 2	$H_g(7)$	6.7
196 ± 2	$H_g(8)$	3.1

Figure 2 shows a high-resolution d^2I/dV^2 spectrum at positive sample bias. Out of the 46 different modes, the set of eight H_g vibrations of a free icosahedral cage nicely matches the observed inelastic excitation peaks (see dashed lines in Figure 2 and Table 1 for a compilation of the peaks and their corresponding change in conductance). The H_g vibrations of a C_{60} molecule describe the set of 5-fold distortions of the icosahedral cage upon addition of one electron into the LUMO and, hence, are JT-active modes.[19] The assignment of the peak at 67 mV is nontrivial because it lies in an energy region with various vibrational modes. Since the A_g modes (at 62 and 184 meV) are also known to have considerable electron−phonon coupling with the LUMO, we may tentatively assign the 67 mV peak to the $A_g(1)$ vibration.[21] However, we cannot exclude that, on the surface, a relaxation of the symmetry selection rules occurs as a result of, for example, charge transfer or some intrinsic distortion of the icosahedral cage, which could allow the excitation of the nonactive $T_{1u}(1)$ vibration.[19,30]

The clear observation of the complete set of H_g modes underlines the importance of JT-type selection rules in IETS and, consequently, of the symmetry character of molecular states close to E_F. Such large vibrational activity contrasts with

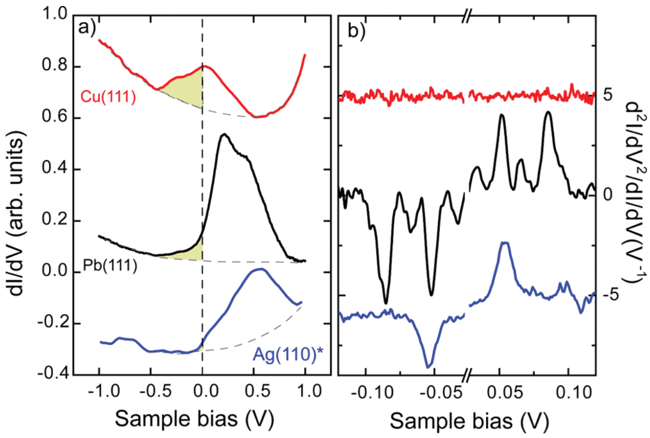

Figure 3. (a) Differential conductance spectra of C_{60} on Cu(111), Pb(111), and Ag(110) [extracted from data shown in 24] (opening feedback loop at $U_b = 2.0$ V, $I_t = 1.2$ nA; $U_b = 2.0$ V, $I_t = 1$ nA; and $U_b = 0.5$ V, $I_t = 0.4$ nA, for Cu, Pb, and Ag, respectively; $U_{mod} = 10$ mV$_{rms}$). The broad peaks correspond to the LUMO-derived resonance of C_{60}, appearing with different degree of Fermi level crossing (shadowed areas). A dashed line is added as a guide background. (b) Normalized and background-subtracted inelastic tunnel spectra of C_{60} on the same three metal surfaces as in panel a.[33]

previous IETS measurements of fullerenes on different metal surfaces.[23−25,31] According to the work of Persson and Baratoff,[12] the proximity of a molecular state to the Fermi level can crucially enhance the inelastic signal in IETS. In this way, the nature of the substrate could influence the vibrational activity of an adsorbate by imposing a certain LUMO alignment with respect to E_F.

To explore the origin of such strong substrate dependence in the vibrational signal, we compare in Figure 3 the differential conductance (dI/dV) and the IETS (d^2I/dV^2) spectra of C_{60} deposited on several metal surfaces: Pb(111), Cu(111) (measured using the same experimental conditions[32]), and Ag(110) (from ref 24). On Pb(111), the dI/dV plot (Figure 4a) shows that the C_{60} LUMO lies only at 0.2 eV above E_F and has a tail crossing the Fermi level. There is a considerable contribution of molecular states to the density of states at E_F, which is consistent with the observation of a complete set of JT active modes in the (off-resonant) inelastic spectra. The Persson and Baratoff model can also explain the lower vibrational signal found for C_{60} on Ag(110), where only one vibrational feature (the $H_g(2)$ mode) was observed: On Ag(110) the LUMO resonance was found mostly unoccupied, at ∼0.5 eV,[24] with very little overlap with E_F. In systems with negligible overlap of the LUMO state with E_F (for example C_{60} on Au(111)), no JT vibrational feature is then expected in the spectra.

Figure 3 also shows that a resonance-mediated excitation model does not necessarily lead to complete vibrational spectra in systems with resonances very close to E_F. On Cu(111), the C_{60} LUMO lies centered at E_F with one of its two subpeaks, tentatively due to the breaking of the fullerene's icosahedral symmetry, located in the negative bias region. However, no inelastic signal at any tip−molecule distance could be detected.[33] The surprising disappearance of the inelastic signal leads us to inquire about possible mechanisms that might reduce the vibrational activity of the fullerene.

It is known that the proximity of molecular resonances to E_F also enhances second-order (vibration emission and absorption) processes, which can partly annihilate the effect of the inelastic channels[12−14] and may even cause a peak-to-dip inversion in the line-shape of some modes.[34] Although this effect could lead to a substantial decrease of the inelastic signal, it can hardly explain by itself a complete featureless spectrum like that in Figure 3b.

The LUMO alignment below E_F on Cu(111) is also accompanied by a change from off-resonant to on-resonant tunneling through the fullerene (e.g., RIETS). When C_{60} is electronically decoupled from a surface, vibronic resonant levels appear in dI/dV plots as a discrete spectrum of sharp peaks decorating the LUMO resonance.[23,21] In our case, C_{60} interacts with the metal and there is a substantial charge transfer leading to the partial occupation of the LUMO. Under these circumstances, molecular vibrations are damped via excitation of electron−hole pairs,[35,36] leading to an intrinsic broadening of their excitation spectrum. An interesting aspect of this resonant regime, mentioned in ref 12, is that the vibrational motion induces charge fluctuations at the interface (i.e., polarons), which can mediate the excitation of additional (dipole active) modes. Nevertheless, the larger line width of the vibronic states in this system is probably the reason of the absence of signal in our IETS data; furthermore, these states contribute themselves to a wider LUMO resonance.[37]

In summary, a rich spectrum of vibrational modes is observed in the IETS spectra of single C_{60} molecules on Pb(111), which remains absent when the fullerene lies on other metal surfaces. The IETS spectra are robust and can be observed with similar shape in both tunnel regime and after the formation of mechanical contact with the STM tip. The modes correspond to the set of JT active vibrations, showing that symmetry selection rules also apply in IETS and can be simply derived from the coupling strength of the molecular modes with the resonance mediating the transport. However, the resulting amplitude of the inelastic signal depends on specific details of the molecule−surface interaction. On the one hand, the proximity of the C_{60} LUMO resonance to E_F in Pb(111) appears to be crucial for the large number of active modes in the spectra. On the other hand, when the LUMO completely overlaps with the Fermi level, the enhanced damping of the vibrational states may obscure their detection in the IET spectra. We believe that these results provide a solid basis for the understanding of inelastic processes in single molecules.

EXPERIMENTAL METHOD

Our measurements have been carried out in a custom-made ultrahigh vacuum (UHV) STM at a temperature of 5 K. A submonolayer amount of C_{60} molecules was sublimated in the UHV on atomically clean Pb(111), Ag(110) and Cu(111) surfaces. Since our transport measurements are performed both in tunnel and in contact regimes, it is important to ensure that the STM tip is formed by the same material as the surface. Indentations of the tip into the bare substrate while applying an elevated tip−sample bias were used to coat it with the substrate material.

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