

Dynamic Jahn-Teller effect in electronic transport through single C₆₀ moleculesThomas Frederiksen,^{1,2,*} Katharina J. Franke,³ Andrés Arnau,^{1,4,5} Gunnar Schulze,³
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Low-temperature scanning tunneling spectroscopy and first-principles calculations are used to characterize electron transport through vibronic states of C₆₀ molecules. This is achieved by positioning a C₆₀ molecule on top of a molecular self-assembled template on Au(111). In these conditions, conductance spectra are shown to reveal the dynamic Jahn-Teller effect of the C₆₀ molecule. This vibronic transport study helps in solving a long-standing debate [Phys. Rev. Lett. **74**, 1875 (1995); Phys. Rev. Lett. **91**, 196402 (2003)] on density-functional calculations of the C₆₀ electron-phonon coupling strength.

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Understanding vibronic coupling effects is of fundamental importance in single-molecule transport junctions.¹ The subject is currently receiving extensive attention from the scientific community.²⁻⁶ The interaction between molecular vibrations and electronic current gives rise to rich transport phenomena. This variety includes detection of vibrational excitations by inelastic tunneling electrons,⁷ progressions of vibrational sidebands in scanning tunneling spectroscopy (STS),⁸ vibrationally induced transitions in photoluminescence,⁹ molecular center-of-mass motion,¹⁰ current-induced fluctuations,¹¹ molecular heating and decomposition,¹² superconductivity,¹³ and metal-insulator transitions.¹⁴ An important factor in governing these effects is the strength of the electronic coupling of the molecule to the metallic leads. If the coupling is strong, the molecular resonances are affected by charge transfer and hybridization, leading to substantial lifetime broadening. On the other hand, if the coupling is weak, the molecule might retain its free-molecule (FM) character.^{15,16}

The C₆₀ molecule is an exceptionally symmetric molecule with highly degenerate electronic and vibrational states.¹⁷ This makes the molecule subject to Jahn-Teller (JT) distortions upon charging,^{14,18,19} and the underlying electron-phonon (*e*-ph) coupled problem results in a complex vibronic fingerprint in the FM excitation spectrum. For instance, the phonon sidebands to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are not expected to appear as multiples of the fundamental frequencies of the modes involved.²⁰ Indeed, such FM vibronic structures have been reported in photoemission spectra of C₆₀ in the gas phase for different charge states of the molecule.²¹⁻²⁵ However, interestingly, these FM features have to our knowledge not yet been observed experimentally in STS, presumably due to difficulties in decoupling C₆₀ sufficiently from its metallic substrate.

Furthermore, the *e*-ph coupled problem in C₆₀ has also attracted substantial theoretical efforts motivated by the discovery of the superconducting phase of alkali doped ful-

lerides A₃C₆₀ and its relation to the “conventional” *e*-ph mechanism.²⁶⁻²⁸ An accurate calculation of the *e*-ph coupling constants is fundamental to such descriptions. In comparison with couplings fitted to photoemission data on C₆₀⁻, it has been argued that couplings derived from density-functional theory (DFT) are too weak.²¹ Contrarily, DFT couplings were later shown to accurately account for photoemission data on C₆₀⁺.²⁴ This apparent controversy calls for complementary studies of the *e*-ph interaction that put DFT-derived couplings to the test.

Here we report on observations of FM fingerprints in conductance spectra of single C₆₀ molecules in a tunneling junction. Fullerenes were decoupled from a Au(111) surface by a template of organic molecules. STS with a low-temperature scanning tunneling microscope (STM) revealed a broad sideband slightly above a sharp LUMO-derived resonance. To understand this, we calculated the vibronic excitation spectrum from first principles. The vibrational modes, frequencies, and *e*-ph couplings were derived from DFT, and the tunneling spectrum was computed numerically by nonequilibrium Green's function (NEGF) techniques as well as by exact diagonalization. The theoretical results explain the origin of the experimentally observed FM fine structure as due to the dynamic JT effect.

To reduce the molecule-substrate coupling experimentally, we used a strategy based on codeposition of C₆₀ and 1,3,5,7-tetraphenyladamantane (TPA) on Au(111), which resulted in spontaneous formation of nanostructures where the C₆₀ cages were lifted away from the surface by support from TPA molecules.^{29,30} One of the observed structural motifs were double rows of alternating TPA and C₆₀ [cf. Fig. 1(a)]. This dielectric template yields troughs in order for single C₆₀ molecules to be trapped between neighboring double rows, as sketched in Fig. 1(b). Differential conductance (*dI/dV* - *V*) spectra taken over the center of these molecules reveal strong nonlinearities around -2.2, 1.3, and 2.5 V, associated with the HOMO, LUMO, and LUMO+1 derived resonances, respectively [Fig. 1(b)]. The corresponding large gap of

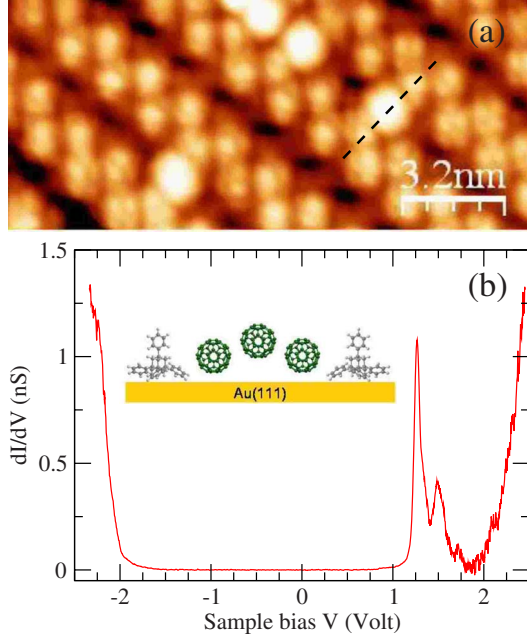


FIG. 1. (Color online) (a) STM image of the double rows of alternating TPA/C₆₀ on Au(111) ($I=16$ pA, $V=580$ mV, and $T=5$ K). Some isolated C₆₀ molecules are adsorbed in the troughs between the rows. (b) Side view of the structural model along the dashed line in (a) and dI/dV spectra recorded on top of such a fullerene ($I_{\text{set}}=0.46$ nA, $V_{\text{set}}=2.5$ V, and $V_{\text{rms}}=14$ mV).

~ 3.5 eV is a clear sign of a molecule weakly interacting with its surroundings.³⁰ Even more striking is the observation of a very sharp LUMO-derived resonance [full width at half maximum (FWHM) (~ 60 meV)] reflecting a long lifetime in the order of 10 fs of the tunneling electron. We also observed a characteristic broad sideband at ~ 230 meV above the LUMO energy, which lies well outside of the 200-meV-wide vibrational spectrum of C₆₀. However, as characteristic for STS experiments, the spectroscopic resolution is better for positive sample biases than for negative ones, and FM details in the HOMO-derived resonance could not be resolved.

Tunneling electrons through a sufficiently decoupled C₆₀ molecule are expected to probe the vibronic spectrum resulting from the intramolecular e -ph interactions. If the transient state of the charged molecule is sufficiently short-lived, the molecule is not statically distorted. Rather, the vibronic spectrum reflects quantum fluctuations among equivalent deformations according to the dynamic JT effect. Near the LUMO-derived resonances in focus here, we can exclude the HOMO and LUMO+1 states from our treatment since these are well separated in energy.¹⁷ Furthermore, group theory gives that only the A_g and H_g intramolecular phonons couple to the t_{1u} LUMO states.²⁰ Thus, the JT problem for C₆₀ is described by the following Hamiltonian:

$$H = \varepsilon_0 \sum_{i=1}^3 c_i^\dagger c_i + \sum_{\nu=1}^{42} \hbar \omega_\nu b_\nu^\dagger b_\nu + \sum_{\nu=1}^{42} \sum_{i=1}^3 \sum_{j=1}^3 M_{i,j}^\nu c_i^\dagger c_j (b_\nu^\dagger + b_\nu), \quad (1)$$

where c_i^\dagger (c_i) is the one-electron creation (annihilation) operator corresponding to one of the three degenerate single-

TABLE I. Partial electron-phonon coupling constants $\lambda_\nu/N(0) = 2/9 \sum_{i,j} |M_{i,j}^\nu|^2 / \hbar \omega_\nu$ of the A_g and H_g intramolecular modes for C₆₀ [cf. Eq. (10) of Ref. 27, with $N(0)$ being the density of states]. The sum of all modes gives a coupling strength of $\lambda^{\text{GGA}}/N(0) = 76.1$ meV (Ref. 33) in good agreement with previous calculations (Refs. 27, 28, 35, and 36).

Mode ν	$\hbar \omega_\nu$ [meV (cm ⁻¹)]	$\lambda_\nu/N(0)$ (meV)	Mode ν	$\hbar \omega_\nu$ [meV (cm ⁻¹)]	$\lambda_\nu/N(0)$ (meV)
$H_g(8)$	195 (1572)	14.6	$H_g(4)$	95 (766)	4.0
$A_g(2)$	185 (1491)	7.3	$H_g(3)$	86 (693)	10.2
$H_g(7)$	178 (1439)	15.0	$A_g(1)$	60 (484)	1.0
$H_g(6)$	155 (1251)	3.2	$H_g(2)$	52 (419)	11.6
$H_g(5)$	136 (1094)	4.3	$H_g(1)$	32 (256)	4.7

particle LUMO states $|i\rangle$, and b_ν^\dagger (b_ν) is the bosonic creation (annihilation) operator of each of the 42 (eight fivefold degenerate H_g and two nondegenerate A_g) vibrational modes ν . The parameters ε_0 , ω_ν , and $M_{i,j}^\nu$ represent the bare LUMO energy, the vibrational frequency of mode ν , and the coupling constant for the scattering of an electron from state $|i\rangle$ to state $|j\rangle$ under creation or annihilation of a phonon in mode ν , respectively. These parameters (see Table I) are obtained from DFT calculations^{31–33} applying the scheme described in Ref. 34 to the neutral,³⁶ isolated C₆₀ molecule. Their values are in good agreement with previous theoretical results found in the literature.^{27,28,35,36}

In our STM configuration the molecule under investigation is more weakly coupled to the tip than to the substrate, i.e., $\Gamma_t \ll \Gamma_s$, in terms of the tip Γ_t and substrate Γ_s tunneling rates. Under this condition the electron occupancy of the molecular states is effectively in equilibrium with the substrate, and the differential conductance at a bias voltage V_s is, to a first approximation proportional, to $\rho(\mu_s + eV_s)\Gamma_t$, where ρ is the local density of states (LDOS). This takes into account both couplings to the leads as well as to the vibrations. We have considered two different methods for calculating ρ : namely, exact diagonalization with the Lanczos scheme (LS) as well as NEGF within the self-consistent Born approximation (SCBA).³⁷

Figure 2(a) shows the computed vibronic spectrum from SCBA for two different values of the total electronic broadening $\Gamma = \Gamma_t + \Gamma_s \approx \Gamma_s$ (FWHM). The spectrum is composed of a main peak followed by a series of sidebands at higher excitation energies. Depending on the broadening, the LUMO spectrum might appear as one main peak with a single sideband separated by 230 meV, similar to the structure reported in photoemission.^{21–24} It is important to realize that the fine structure in the LDOS does not relate in a simple way to the fundamental frequencies of the A_g and H_g modes (in the range of 32–195 meV as indicated with vertical dotted lines in Fig. 2). Hence, for JT systems it is not possible to directly relate vibronic structure in spectroscopy with molecular frequencies.

To gain an understanding of the contributions from different vibrational modes to the total spectrum, we show in Fig. 2(b) the LDOS as resulting from a calculation with coupling to only one type of mode at a time. Although the sideband

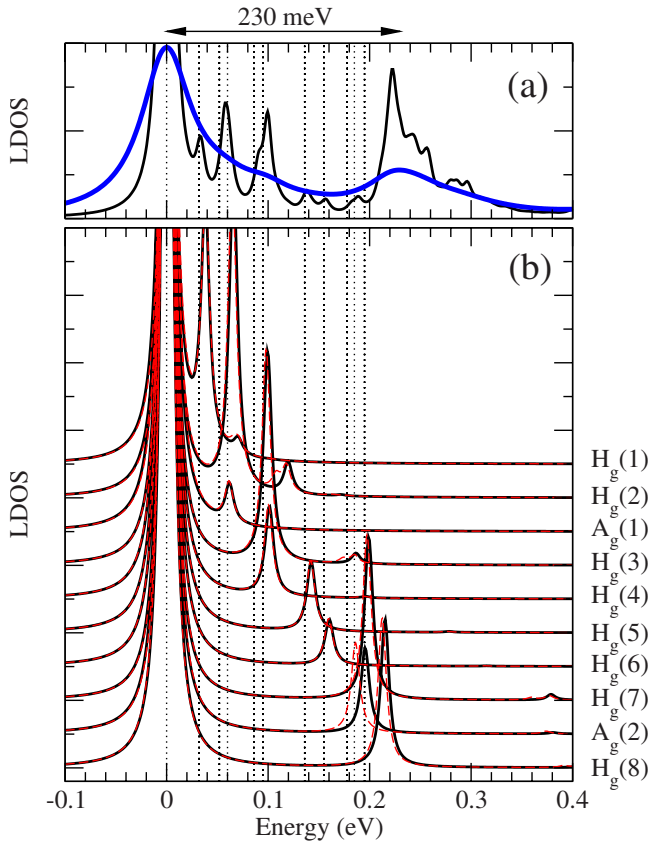


FIG. 2. (Color online) (a) Theoretically computed JT-induced fine structure in the LDOS of the LUMO via coupling to A_g and H_g modes, shown for two different intrinsic level broadenings: $\Gamma=10$ meV (black line) and $\Gamma=60$ meV (thick blue/dark gray line). (b) Analysis of the position of the phonon sidebands including only one mode at the same time, calculated with both the SCBA (black lines) and LS (dashed red/gray lines) methods ($\Gamma=10$ meV). For clarity the spectra are offset and shifted to place the main peak at zero energy. The vertical dotted lines indicate the fundamental frequencies of the A_g and H_g modes.

structure is much simpler, one observes that the peak separation for all H_g modes is larger than the phonon energy. This nontrivial behavior is generic to the $T_{1u} \otimes h_g$ JT problem.²⁰ Figure 2(b) also shows that, except for the more strongly coupled $A_g(2)$ mode, SCBA and LS yield essentially the same results for the LDOS due to the weak e -ph couplings.

Next, we turn to a comparison with the experiment. The measured tunneling spectra on different molecules exhibit certain variations in peak position and structure around the LUMO resonance. This variation is likely due to slightly different environments, and possibly also molecular orientation, of the selected C_{60} species. In Fig. 3 we compare the dI/dV spectra of three different molecules with theoretical spectra by applying an appropriate substrate coupling Γ . The relative peak height as well as the position of the sideband with respect to the main peak are in very good agreement. This fact supports the interpretation that these spectra indeed exhibit the FM signature resulting from the dynamic JT effect.

Alternative mechanisms, such as the weak spin-orbit coupling in carbon¹⁷ or the Stark effect from the applied voltage,

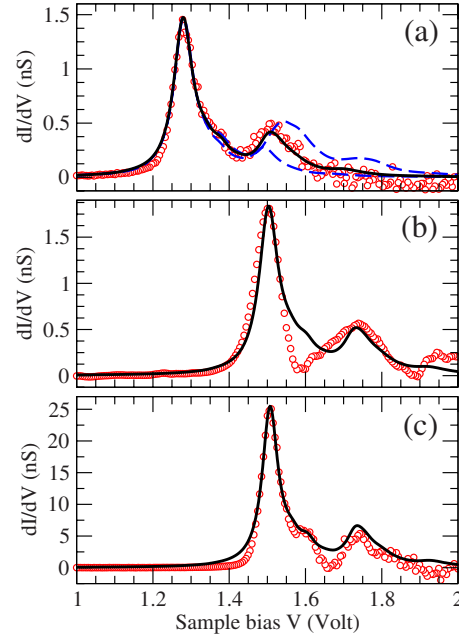


FIG. 3. (Color online) Direct comparison between experiment (red/gray circles) and theory (black line) for three different molecules: (a) $I_{\text{set}}=0.3$ nA, $V_{\text{set}}=2.5$ V, $V_{\text{rms}}=7$ mV, and $\Gamma_s=60$ meV; (b) $I_{\text{set}}=0.52$ nA, $V_{\text{set}}=2.5$ V, $V_{\text{rms}}=3.5$ mV, and $\Gamma_s=60$ meV; (c) $I_{\text{set}}=1.2$ nA, $V_{\text{set}}=2.5$ V, $V_{\text{rms}}=7$ mV, and $\Gamma_s=50$ meV. Panel (a) includes calculations with scaled e -ph coupling constants (dashed blue/dark gray lines) corresponding to $\lambda_\nu \rightarrow 1/2\lambda_\nu^{\text{GGA}}$ and $\lambda_\nu \rightarrow 2\lambda_\nu^{\text{GGA}}$.

cannot account for the 230 meV splitting seen in Fig. 3. Although details in the weak electronic coupling of the C_{60} molecule to its environment may have an influence in the experimentally recorded spectra, we believe that this effect solely cannot produce such an agreement as the JT theory presented above for a decoupled molecule. Furthermore, from the different time scales of electron-tunneling events and residence times in the molecule, we can also exclude heating effects. Based on the NEGF-SCBA calculations, we found that heating would be important if the current through the LUMO states were raised by two orders of magnitude.

In Fig. 3(a) we also show how the calculated spectrum changes by a scaling of the DFT-derived e -ph couplings corresponding to $\lambda_\nu \rightarrow 1/2\lambda_\nu^{\text{GGA}}$ and $\lambda_\nu \rightarrow 2\lambda_\nu^{\text{GGA}}$. As seen, these scalings decimate the agreement with experiment in terms of peak ratio and separation, thus pointing toward reasonable values of the e -ph coupling strength within DFT.

In summary, low-temperature STM dI/dV spectra recorded under an experimental preparation procedure of codeposition of C_{60} and TPA molecules on Au(111) revealed a delicate fine structure around the LUMO-derived resonance interpreted as due to the dynamic JT effect. The quantitative agreement between experimental and theoretical spectra further supports that the calculated e -ph couplings from DFT provide an accurate description for the vibrational interactions in the molecule. Furthermore, our simulations predict that similar effects appear when tunneling through other resonant levels, thus suggesting that JT phenomena need to be taken into account to understand transport through mo-

lecular species in the weakly coupled regime.

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