Phonons and conduction in molecular quantum dots: Density functional calculations of Franck-Condon emission rates for bifullerenes in external fields

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We report the calculation of various phonon overlaps and their corresponding phonon emission probabilities for the problem of an electron tunneling onto and off of the fullerene-dimer molecular quantum dots C_{72} and C_{140}, both with and without the influence of an external field. We show that the stretch mode of the two balls of the dumbbell couples most strongly to the electronic transition and, in turn, that a field in the direction of the bond between the two fullerene balls is most effective at further increasing the phonon emission into the stretch mode. As the field is increased, phonon emission increases in probability with an accompanying decrease in probability of the dot remaining in the ground vibrational state. We also present a simple model to estimate the effect of molecular size on the phonon emission of composite dimer molecules and compare the results with the complete analysis of C_{72} and the experimentally tested C_{140}. In our approach we do not assume that the Hessians of the molecule are identical for different charge states. Our treatment is hence a generalization of the traditional phonon overlap calculations for coupled electron-photon transitions in solids.

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I. INTRODUCTION

Physics is full of examples of phonon-coupled quantum tunneling events. A classic example from the 1960s is the work done with trapped-electron color centers in the lattices of the alkali halides.\textsuperscript{1} More modern examples include the study of how the mobility of interstitials in metals is modulated by coupling of the defect to the resulting distortion of the surrounding lattice\textsuperscript{2} and the study of how the interchain hopping by polarons is affected by phonon interactions.\textsuperscript{3} In these studies and others, the frequencies before and after the transition were assumed to be unchanged and only the coordinate about which the harmonic potential is centered shifts. Here, our use of the word phonon, traditionally used for plane-wave-like solutions in periodic crystals, for vibrational normal mode is in the same spirit in this context for which we use the term quantum dot, a macroscale object, for molecule.

Over the past several years, several experiments and theoretical studies\textsuperscript{4–6} have been done where single molecules have been used as the medium for vibration-assisted tunneling. Some recent experimental examples are measurements done with scanning tunneling microscopes,\textsuperscript{7,8} studies of single hydrogen molecules in mechanical break junctions,\textsuperscript{9} and the investigations that have directly motivated this work,\textsuperscript{10,11} where a single molecule is deposited between two leads and is subjected to both a source drain and gate bias. This is done in the Coulomb blockade regime, where the bias is tuned so that sequential transport can occur and a differential conductance graph can be plotted. In many of these differential conductance graphs, in addition to the main lines due to the change in the charge state of the molecule, there are a series of sidebands thought to be caused by the coupling of the electron to the vibrational modes of the molecule.

Spectroscopy has long been utilized as a tool in both chemistry and physics to study the properties and structure of atoms and molecules. Different types of spectroscopy are used for different aims; optical spectroscopy, for example, studies the interaction of electromagnetic radiation with the sample while this paper addresses the differential tunneling spectroscopy described above. Franck-Condon factors\textsuperscript{12} serve as a very good tool for analyzing the absorption and emission band intensities corresponding to vibrational levels in atoms and molecules.\textsuperscript{13} Over the years, many such molecular vibrational spectra have been calculated and cataloged using Franck-Condon factors.\textsuperscript{14,15} Single-molecule transistors offer an opportunity to apply the Franck-Condon principles to a new system. Because we are dealing with single molecules, we can calculate [using \textit{ab initio} density functional theory (DFT)] the full vibrational profile of both the initial and final electronic states of the molecule and thus calculate the Franck-Condon intensities generally.

In this paper, we use a general theory for vibrational overlaps where the vibrational modes of both the initial and final electronic states of the molecule are considered. Charge-dependent Hessians and anharmonic potentials in the context of single-molecule transistors have been considered previously\textsuperscript{16,17} where the molecule is assumed to have one dominant mode in each electronic state. In the field of chemical spectroscopy, this topic has been addressed\textsuperscript{18} through a general consideration of the Franck Condon factors with Duschinsky rotation\textsuperscript{21} and its refinements,\textsuperscript{22,23} which allows for different frequencies and eigenvectors between different charged states. Our paper considers a realistic model of an N-atom molecule with 3N possible modes (for example, the bifullerene C_{72} with 216 possible modes; see Fig. 1) and allows the calculation of experimental scenarios by combining our formulation with results from density functional theory.

In Sec. II, we set up our Hamiltonian. In Sec. III, we outline our version of the phonon overlap calculations including the Duschinsky rotation. In Sec. IV, we outline our DFT numerical methods. Section VI calculates the zero-field overlaps. Section VII addresses the overlaps in a field. Section VIII introduces a simple two-ball-and-spring model for
III. PHONON OVERLAP INTEGRALS

Phonon overlap integrals arise in quantum transitions in a variety of contexts, as described in the Introduction. We are interested in transitions between two electronic states in a bifullerene molecule and how the transition is affected by the change in relaxation of the positions of the neighboring atoms. Within the Born-Oppenheimer approximation, the total wave function is described by \( \Psi(z) = \phi(z) \phi(x) \), where \( x \) labels the nuclear coordinates as above and \( z \) labels the electron coordinates. Strictly speaking, the ground-state electron wave function depends parameterically on the nuclear positions \( x \), but for the bifullerenes the zero-point atomic fluctuations \( \Delta x \) are on the order of picometers where tunneling matrix elements vary on angstrom scale. Hence we can assume \( \phi(x) = \phi(z) \) and hence factor our wave function into a purely electronic component and a purely nuclear component. [This corresponds to the approximation in Eq. (4) that the tunneling matrix element \( T^{vr} \) is independent of the atomic positions \( x \).] A quantum transition mediated by a perturbing Hamiltonian \( \hat{H}^{(m)} \) involving only electronic degrees of freedom [such as in Eq. (4)] will thus be given by

\[
\langle \Psi_f(z,x) | \hat{H}^{(m)} | \Psi_i(z,x) \rangle = \langle \phi(z) \phi(x) | \hat{H}^{(m)} | \phi(z) \phi(x) \rangle = \langle \phi(z) | \hat{H}^{(m)} | \phi(z) \rangle \langle \phi(x) | \phi(x) \rangle.
\]

Conductance through our molecular quantum dot demands an electronic transition onto the dot (potentially exciting vibrations), followed by a transition off of the dot. We imagine that these two transitions are incoherent, that the bottleneck is tunneling from the right lead onto the dot, and that the vibrational excitations thermalize before the next transition. For simplicity, we also assume zero temperature and low currents (so that nonequilibrium vibrational excitations may be ignored). All of these assumptions are thought to be fairly accurate for the experimental system. With these assumptions, the conductance through the dot, expressed in Beenakker’s notation, is a sum of the conductances through parallel “channels” with different final phonon excitations

\[
\text{ conductance } \propto \sum_{E_p < eV} \Gamma_p \propto \sum_{E_p < eV} |\langle \phi_p(x) | \phi(x) \rangle|^2.
\]

Here \( eV \) is the energy available to add an electron to the dot under external voltage \( V \), \( E_p = e_d + \Sigma_{\nu} P_{\nu} \hbar \omega_\nu \) is the energy of the eigenstate of the dot Hamiltonian [Eq. (3)] with \( P_n \) phonons emitted into mode \( n \), and the conductance \( \Gamma_p \) from the right lead onto the dot through channel \( p \) involves the square of the matrix element \( T^{vr}_{p} \) of Eq. (5), and hence the square of the phonon overlap from the neutral ground state


\[ \phi' \] into the excited vibrational state \( \phi'_f \) of the charged molecule. As each threshold step in bias is crossed, a new possible pathway becomes accessible and the square of its overlap must be added to the expression.

This expression for the conductance is used in calculations described in Sec. IX to predict I-V relations for the molecular quantum dot (see Fig. 10 below). The general theory includes finite temperatures, more symmetric tations described in Sec. IX to predict lap must be added to the expression.

As each threshold step in bias is crossed, a new pos-

\[ \text{sec.} \]

between the initial vibrational state of the initial charge state since it modulates the total transition rate. Its value is a mea-

lack of coupling to a substrate may account for this increase. In other experiments, the experimental setup was arranged

pended carbon nanotubes. However, the authors note that the

In recent experiments, long phonon lifetimes extending at least 50 times beyond the lifetimes observed in Raman spectroscopy have been measured for experiments on suspended carbon nanotubes. However, the authors note that the

In this section we calculate the transition rate from the

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\[ \text{PHONONS AND CONDUCTION IN MOLECULAR QUANTUM} \]

\[ \text{PHYSICAL REVIEW B} \]

\[ \text{045435} \]

\[ \text{045435-3} \]
We want to express the single Gaussian as one that is centered on a new origin $y_{\text{max}}=\Delta$ with a new Hessian $\Omega$ so that the integral is of the form

$$\int d(y-\Delta)e^{-(1/\hbar)(y-\Delta)^\dagger\Omega(y-\Delta)+B},$$

which we know how to solve. Here $B$ is one of the unknowns we are solving for, a constant which will be pulled out of the integral with a value given in Eq. (17).

Setting like quantities equal between expressions (15) and (16), we obtain

$$\Delta = (\Omega_1 + \Omega_2)^{-1}\Omega_2 \Delta,$$
$$\Omega = \frac{1}{2}(\Omega_1 + \Omega_2).$$

Our overlap integral now looks like

$$\int d(y-\bar{\Delta}(y-\bar{\Delta})^\dagger\bar{\Omega}(y-\bar{\Delta})]e^{-(1/\hbar)(y-\bar{\Delta})^\dagger\bar{\Omega}(y-\bar{\Delta})}\Delta^\dagger\Omega_2 \Delta.$$

Rewriting the constant part of the integral in terms of $\bar{\Omega}$ and $\bar{\Delta}$, we have

$$\int d(y-\bar{\Delta}(y-\bar{\Delta})^\dagger\bar{\Omega}(y-\bar{\Delta})]e^{-(1/\hbar)(y-\bar{\Delta})^\dagger\bar{\Omega}(y-\bar{\Delta})}\Delta^\dagger\Omega_2 \Delta.$$

Changing variables to $\bar{y} = y - \bar{\Delta}$, this last integral is another multidimensional Gaussian, equaling $1/N\tilde{\Omega}$, where $\tilde{\Omega} = \sqrt{\text{det}(\Omega/\hbar)}$. The ground-state to ground-state overlap is then

$$O_{0,0} = \frac{N_1N_2}{\tilde{N}^2}\exp\left(\frac{1}{\hbar}\bar{\Delta}^\dagger\bar{\Omega}\bar{\Delta}\right)\exp\left(-\Delta^\dagger\Omega_2 \Delta/2\hbar\right).$$

The probability of being left in the phonon ground state, the tunneling rate $\Gamma$, and the conductance are all suppressed by a factor $\exp(-G) = |O_{0,0}|^2$, where

$$G = -\ln(|O_{0,0}|^2).$$

This defines the total $g$ factor which we will use to characterize the overall strength of the phonon coupling.

We can similarly calculate the overlap between the ground initial state and a final state with one phonon excited into mode $\alpha$:
vanish. initial state and the excited final state is specifically changed. It is well known that the total overlap integral is the phonon frequencies and normal modes remain un-

\[
O_{0,1a} = \int dy \Psi_n^{(1)}(y)\Psi_n^{(2)}(y - \Delta) \\
= \int dy \left[ N_f e^{-\frac{1}{2}h}(y - \Delta) \cdot \tilde{\Psi}_n^{(2)} \right] \\
\times \exp \left( \frac{-1}{2h} (y - \Delta)^2 \Omega_n (y - \Delta) \right).
\]

Combining the exponentials, rewriting them in terms of \( \tilde{\Omega} \) and \( \Delta \), we find

\[
O_{0,1a} = N_f N_2 \int dy \left[ \sqrt{2 \omega_f / \hbar} (y - \Delta) \cdot \tilde{\Psi}_n^{(2)} \right] \\
\times e^{-\frac{1}{2}h}(y - \Delta) \Omega_n (y - \Delta) e^{-\frac{1}{2}h}(y - \Delta)^2 \Omega_n (y - \Delta) \Omega_n (y - \Delta).
\]

Changing the variables to \( \tilde{y} = y - \Delta \), we have

\[
O_{0,1a} = N_f N_2 \int d\tilde{y} \left[ \sqrt{2 \omega_f / \hbar} (\tilde{y} - \Delta) \cdot \tilde{\Psi}_n^{(2)} \right] \\
\times e^{-\frac{1}{2}h}(\tilde{y} - \Delta) \Omega_n (\tilde{y} - \Delta) e^{-\frac{1}{2}h}(\tilde{y} - \Delta)^2 \Omega_n (\tilde{y} - \Delta) \Omega_n (\tilde{y} - \Delta).
\]

(22)

Since the first term in the last integral is odd in \( \tilde{y} \), it must vanish.

Hence, from Eq. (20), the overlap between the ground initial state and the excited final state is

\[
O_{0,1a} = O_{0,0} \left( \sqrt{2 \omega_f / \hbar} [\tilde{\Psi}_n^{(2)} \cdot (\tilde{\Delta} - \Delta)] \right).
\]

(23)

We define

\[
g_a = \frac{|O_{0,1a}|^2}{|O_{0,0}|^2} = \frac{P_a}{P_{ground}} = \frac{\Delta I_a}{\Delta I_{ground}},
\]

(24)

which experimentally gives the ratio of the current flowing emitting one phonon in mode \( \alpha \) per electron to the current emitting zero phonons (the ratio of the step heights in the \( df/dV \) curves). Thus,

\[
g_a = \left( \sqrt{2 \omega_f / \hbar} [\tilde{\Psi}_n^{(2)} \cdot (\tilde{\Delta} - \Delta)] \right)^2.
\]

(25)

In the special case \( \Omega_1 = \Omega_2 \), where the change in charge state does not alter the spring constant matrices \( K_1 \) and \( K_2 \), the phonon frequencies and normal modes remain unchanged. It is well known that the total overlap integral is related to the one-phonon emission rates in a simple way: specifically \( G = \Sigma_{\alpha \beta} g_{\alpha \beta} \). This is no longer the case when the two charge states have different spring constant matrices: we must calculate them explicitly. The probability of multiple phonons being emitted into distinct phonon modes is given by \( g_{\alpha \beta} \cdot |O_{0,0}|^2 \), as it is for the traditionally studied case \( \Omega_1 = \Omega_2 \). But the probability for \( n \) phonons to be emitted into the same final state is no longer \( g_{\alpha \beta} \cdot |O_{0,0}|^2 \). We do the calculation of two phonons in the Appendix; more general Duschinsky rotation calculations can be found in the literature.

IV. METHODS

We used GAUSSIAN2003, a quantum chemistry package, to calculate all of the quantities needed in our calculation. These quantities include the force constant matrix \( K \) for different charge states of the molecule with dimension \( 3N \times 3N \). This matrix is related to the \( \Omega \) matrix by the equation \( K = M \Omega M \Omega \) since in the cases of both \( C_{140} \) and \( C_{72} \), \( M \) commutes with \( \Omega \). (Remember, in our notation, \( \Omega \) is the frequency matrix squared.) We obtain the vibration frequency eigenvalues and normal-mode eigenvectors from \( \Omega \).

The program also gives the geometrically minimized structures of the molecule for its different charge states \( r \) and the forces on the atoms \( f \) under the influence of an external electric field.

All quantities are calculated under the hybrid B3LYP level of theory of the DFT model. Because we were working with molecules of considerable size and were calculating vibrational modes which require many electronic relaxation calculations, we used the minimal STO-3G basis set for our larger molecule \( (N=140) \) and the slightly larger \( 3-21G^* \) basis set for our smaller molecule \( (N=72) \). Comparisons between the two basis sets for \( C_{72} \) suggest that the qualitative features are similar; more complete basis sets capture the polarization and charging effects more accurately which serve to increase our \( g \) factors since the variation between neutral and charged species are more pronounced. Our analytic approaches and their aim are independent of the details of the quantum chemistry calculation. All matrix calculations are done under MATLAB or its freeware clone GNU OCTAVE.

V. MOLECULES AND THEIR MODES

Our studies were inspired by work done by the McEuen and Ralph groups at Cornell and Berkeley. Specifically, we looked at the single-molecule transistor made up of \( C_{140} \), a molecule whose vibrational modes have been modeled and studied experimentally by Raman spectroscopy. \( C_{140} \) is comprised of two \( C_{70} \) fullerene cages covalently bonded to each other via two \( C-C \) bonds. The dominant mode is the low-energy intercage vibration stretch mode at 11 meV shown schematically in Fig. 4. The second molecule studied was based on our interest in \( C_{140} \). We wanted a molecule with similar properties to \( C_{140} \), but with fewer atoms \( (C_{72}) \). The aim was to increase the accuracy of the basis set used for calculations which would be computationally costly with larger molecules.

Like \( C_{140} \), the dominant excited mode was the intercage stretch mode which has an energy of 19 meV in \( C_{72} \). The molecule is depicted in Fig. 1. Figures 1 and 4 were produced using GAUSSIAN2003 to minimize the geometry of the molecule and RASMOL to plot the atom positions.

For both molecules, the low-energy modes correspond to large-scale motion of the molecules such as the bending,
twisting, or stretching of the two cages with respect to each other (acoustic-type vibrations) while higher-energy modes correspond to motion of the atoms on a smaller scale (optical-type vibrations). For example, for C$_{140}$ the 15-meV mode corresponds to a seesaw motion of the two cages with respect to each other and the 17-meV mode corresponds to a twisting motion of the two cages away from a central point, while the higher-energy 78-meV mode corresponds to simultaneous deformation of the cages themselves. The vibrations GAUSSIAN calculates are within 5% of the experimental values.

VI. BASIC QUANTITIES

The shift in the geometrically minimized structure of the C$_{140}$ molecule as it acquires an extra electron is the predominant factor in determining the amount of phonon emission. If the structure changes little, the overlap between the two ground vibrational states of the initial and final charge states of the molecule will be larger, which suppresses phonon emission since the overlap is a mathematical statement of how likely it is for the molecule to remain in the ground vibrational state rather than transitioning to an excited vibrational state.

It is not known what the natural charge states of our molecule are on a gold substrate, as used in the experiments we compare to. A single C$_{60}$ molecule typically has charge $-2e$ on gold; doubling this, we anticipate that the case of interest may involve a transition from perhaps four to five extra electrons on our molecule.

Table I is a chart of the change in the intercage distance between the two centers of masses of the fullerene cages upon adding an electron. As one can see, the distance increment increases as the charges increases. Therefore, as the charge on the molecule increases, the molecular incremental distortion $\Delta r$ increases, and consequently the probability that the molecule will remain in the ground vibrational state after an electron has hopped on decreases, leading to stronger phonon sidebands in the differential conductance graphs. Table II gives, for each electronic transition of the molecule up to a charge state of four extra electrons, the total $g$ factors [Eq. (21)] in the absence of an applied field, the $g$ factor associated with the first excited state [Eq. (25)] where an intercage stretch-mode phonon is emitted, the probability of the molecule remaining in the ground state ($|O_{0,0}|^2$), and the probability that the molecule’s final vibrational state is the first excited state of the stretch mode ($|O_{0,1}\alpha\omega\text{stretch}|^2$).

Plotting a graph of the $g_\alpha$ factor for the electronic transition of a neutral molecule to 1 molecule versus all 216 modes (as in Fig. 5) confirms that the stretch mode of the molecule dominates single-phonon emission. We also plot the corresponding graph of $g_\alpha$ for C$_{140}$ in Fig. 6. As the charge state increases, the effects and phonon sideband strengths will increase.

Again, it is the stretch mode (whose identity is confirmed by displacing the equilibrium coordinates of the molecule by a distortion that is proportional to the eigenmode) that is important. Two-phonon emission may also be significant since experimentally there is sometimes a second smaller peak at 22 meV which may be due to two-phonon emission.

**Table I.** Change in distances ($\Delta r$) between centers of mass of the fullerene cages for C$_{140}$ during different charge transitions ($Q_1 \rightarrow Q_2$) where $Q_1$ is the initial charge state of the molecule and $Q_2$ is the final charge state of the molecule. Shown are the results of our DFT simulations and those of our simple model (Sec. VIII).

<table>
<thead>
<tr>
<th>Transition $Q_1 \rightarrow Q_2$</th>
<th>DFT $\Delta r$ [pm]</th>
<th>Simple $\Delta r \approx s(Q_2) - s(Q_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 $\rightarrow$ 1</td>
<td>1.005</td>
<td>3.16</td>
</tr>
<tr>
<td>1 $\rightarrow$ 2</td>
<td>1.794</td>
<td>9.26</td>
</tr>
<tr>
<td>2 $\rightarrow$ 3</td>
<td>2.333</td>
<td>14.8</td>
</tr>
<tr>
<td>3 $\rightarrow$ 4</td>
<td>3.056</td>
<td>19.5</td>
</tr>
<tr>
<td>4 $\rightarrow$ 5</td>
<td>3.7337</td>
<td>23.4</td>
</tr>
</tbody>
</table>

**Table II.** C$_{72}$ undergoing different transitions. Probabilities and $g$ factors for different transitions. For convenience we include columns 4 and 5; their result can be deduced from the second and third columns.

| Transition | $G$ | $g_{\text{stretch}}$ | $|O_{0,0}|^2$ | $|O_{0,1}\alpha\omega\text{stretch}|^2$ |
|------------|-----|----------------------|--------------|----------------------------------------|
| 0 $\rightarrow$ 1 | 0.960 | 0.33 | 0.38 | 0.125 |
| 1 $\rightarrow$ 2 | 1.18 | 0.406 | 0.31 | 0.126 |
| 2 $\rightarrow$ 3 | 1.27 | 0.455 | 0.28 | 0.127 |
| 3 $\rightarrow$ 4 | 1.29 | 0.492 | 0.27 | 0.135 |

**FIG. 4.** C$_{140}$ with stretch mode shown schematically.

**FIG. 5.** $g_\alpha$ for the C$_{72}$ 0 $\rightarrow$ 1 charge-state transition. The large peak is the stretch mode at 19 meV. Including the two-state emission lines would add an additional peak at 38 meV (twice the stretch mode) and an otherwise roughly continuous background (see Fig. 10).
The only significant two-phonon line is at 22 meV. Two-phonon emission, however, yields a small contribution to the conductance. For two phonons emitted into the same mode, the contribution is given by the product of the single-phonon overlaps. For two phonons emitted into different modes, the contribution cannot be simply described by such a product and a complete expression obtained from integrating the product of the relevant multidimensional Gaussians is needed. Although we can calculate the probability of a transition to 2-phonon up to $n$-phonon vibrational final states, we confine ourselves to one-phonon emission in our calculations because, as will be illustrated in Fig. 10, two-phonon emission contributes a continuous background with the only sizable jump from the 11-meV mode.

VII. CONSIDERING EXTERNAL ELECTRIC FIELDS

In reality, the molecule is not in a vacuum but in a real environment of leads, substrate, and counter-ions. In the experiments, there is a range of $g$ factors for different experiments involving the same molecule. This implies that environmental effects play an important role and motivates our calculation of $g$ factors in the presence of external fields. We account for one feature of this variable environment by applying an electric field to the system. This external field can come about as a result of image charges that are set up across the substrate or across the leads when extra electrons are added to the quantum molecular dot.

In the GAUSSIAN2003 program, we can impose an external field, relax the electronic wave function due to the induced polarization, and measure the force (expressed as a 3$N$-vector, in this case a 216-vector) on each atom. The external field will polarize the charge on the molecule as seen in the following representation in Fig. 7 of the highest occupied molecular orbital level of C$_{140}$ under an electric field of $4 \times 10^4$ V/m along an intercage bond, showing the polarization of the electron density.

11-meV line for C$_{140}$ increases substantially under an external field.

As can be seen in the plot, the field does increase the $g$ factor from its bare value. At reasonable fields (those that we might expect to find in the experimental literature) such as the region where the field $\approx 3 \times 10^5$ V/m, $g_\alpha$ for the most represented mode (the stretch mode) increases to about 0.5. This field would correspond to a charge placed 7 Å away. And for a field corresponding to a charge placed 6 Å away (the closest plausible distance), $g_\alpha$ becomes around 1.0. However, in experiments, the $g$ factor varies from values of much less than 1 to values as high as 6. In order to reach these quantities in our present theory, we would need to impose much higher and unphysical fields.

Another dependence we examined was the $g$-factor dependence of the various modes on the angle of a fixed electric field. In Fig. 9, the electric field was fixed at an extremely high value of $5 \times 10^{12}$ V/m. The leftmost figure is the 11-meV mode—the stretch mode. Following it from left to right are the 3.7-meV mode magnified by a factor of 20,000, the 2.37-meV mode magnified by a factor of 20, the 15-meV mode magnified by a factor of 5, the 17-meV mode magnified by a factor of 200, and finally the 27.6-meV mode magnified by a factor of 500.

The molecule is oriented such that its long axis is aligned vertically. From the figure, we see that there is no coupling of the stretch mode (left shape) to the field when the field is aligned in a direction perpendicular to the stretch mode and that there is maximum coupling in the direction parallel to...
the field. C140 has C2
symmetries of the plots in Fig. 9 reflects the symmetry of the
rotation of angle
to second order in
is the equilibrium distance of the spring,
is the Coulomb constant.
We also note that \( M_{\text{total}} = M_{\text{ball}_1} + M_{\text{ball}_2} = 2M_{\text{ball}} \) and \( M_{\text{red}} = \frac{M_{\text{ball}_1}M_{\text{ball}_2}}{M_{\text{ball}_1} + M_{\text{ball}_2}} = M_{\text{ball}}/2 \) are the well-known center of mass and
reduced mass for the system. The last assignments we make
are expressions for the charges on each ball (\( q_1 \) and \( q_2 \)) in
terms of the charges in the system:

\[
q_1 = \frac{Q}{2} + \frac{q}{2},
q_2 = \frac{Q}{2} - \frac{q}{2},
\]

where \( Q \) is the total charge of the system and \( q \) is the
difference between the charges on the two balls. The potential
energy \( U \) then becomes

\[
U = E_{\text{spring}} + E_{\text{field}} + E_{\text{Coulomb}} + E_{\text{capacitance}}
= \frac{1}{4r(a + x)} \left\{ -2a^2E qr + K[q^2(x - r) + Q^2(x + r)] \right.
+ 2r(2EQX - Eqx + kx^2)
+ a[K(q^2 + Q^2) + 2r(2EQX - 2Eqx + kx^2)] \right\}.
\]

Here \( x = x_2 - x_1 \) is the relative distance between the two balls and \( X = \frac{x_1 + x_2}{2} \) is the center of mass coordinates of the system.
We next take the derivative of the potential with respect to \( q \)
as the difference in charges on the two balls and set the
resulting expression \( \frac{\partial U}{\partial q} \) equal to zero. Solving this expression for \( q \) gives us the minimized distribution of charges on the
balls under an external field:

\[
q = \frac{Er(a + x)^2}{K(a - r + x)}. \tag{29}
\]

Similarly, we take the derivative of the potential energy \( U \) with respect to the deviation of the stretch coordinate from equilibrium \( x \), set this expression equal to zero, and solve for \( x \). We keep terms up to second order in \( Q \) and \( E \) and get

\[
x(Q) = AE^2 + BQ^2 + CE^2Q^2, \tag{30}
\]

where \( A \), \( B \), and \( C \) are given by

\[
A = \left( \frac{2a^2 - 5ar - 3r^2}{4kK(a - r)^3} \right) ra^2, \quad B = \frac{K(a^2 + r^2 - 2ar)}{4a^2k(a - r)^2}, \quad C = \left( \frac{2r - a}{8(a - r)^5} \right) r. \tag{31}
\]

In Table I, we compare the \( \Delta r = x(Q_2) - x(Q_1) \) in the absence of a field for our simple model and the full DFT calculation discussed earlier where \( Q_1 \) is the total charge for the initial system and \( Q_2 \) is the total charge for the final system. The simple model has between 3 and 6 times the
distortion of the quantum chemistry calculation, likely due to
a combination of more effective screening of the Coulomb
FIG. 10. I-V curve predicted for C72 for one-phonon processes (solid line) and up to two-phonon processes (approximate, dashed line), using the DFT STO-3G basis set. The arrow indicates the position of the two-phonon contribution from the stretch mode.

FIG. 10 shows the current divided by $I_0$ versus the available energy above the ground-state to ground-state threshold for both one-phonon emission processes (solid line) and up to two-phonon processes (dashed line). The plots are constructed by iteratively calculating phonon emission from a pool of available energy. As energy decreases, less is available for emitting phonons. Our $g_a$'s make use of the fact that the phonon quadratic forms $\Omega$ change between different charge states. As one can see, the currents due to one-phonon processes and for up to two phonon processes share similar gross features at the beginning such as the jump in current at the 19-meV energy mode corresponding to the stretch mode of the molecule. However, they start to deviate as the energy increases until they level off at different values of the current (0.8 for the one-phonon process and 0.95 for the two-phonon processes) which would seem to indicate that two-phonon processes will play a role in the I-V characteristics of a molecular quantum dot.

In addition, the I-V curve that includes all $n$-phonon processes will asymptote to 1. The two-phonon contribution forms almost a continuous background, except for $2\omega_{\text{stretch}}$, whose position is shown with an arrow in Fig. 10. We also note that the our treatment of two-identical-phonon emission is (for convenience) not the correct formula derived in Eq. (A14) which allows the frequencies to change between the initial and final states, but that would take us beyond our current illustrative goal.

\[ O_{0,2a} = e^{-C_{g_a}^2/2}, \]

\[ II_0(E) = \sum_{a} \left[ O_{0,1a} \Theta(E - h\omega_a) + O_{0,2a} \Theta(E - 2h\omega_a) \right] + \sum_{a,a' \neq a} O_{0,1a1a'} \Theta(E - h\omega_a - h\omega_{a'}). \]

X. CONCLUSION

There is much recent interest in vibrating mechanical systems coupled to electron transport on the nanoscale, from nanomechanical resonators to single-electron shuttles. Vibrational effects on electron transport through molecules have been studied since the 1960s in devices containing many molecules and more recently have been shown to be important in transport through single molecules measured using scanning tunneling microscopes, single-molecule transistors, and mechanical break junctions. In a natural extension of work done in the 1920s by Franck, Condon, and others in atomic spectra, we have studied the effects of molecular vibrations on electron transport through a molecule. We have shown that density functional theory calculations of the normal modes and deformations, coupled to a straightforward linear algebra calculation, can provide quantitative predictions for the entire differential tunneling spectrum, even including external fields from the molecular environment.

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APPENDIX

Here we show how one can calculate the Franck-Condon factor for a transition from the neutral ground state to an excited state with one vibrational mode in a doubly excited state. (For emission into general excited states, we would need to use the appropriate multidimensional Gaussian multiplied by the appropriate Hermite polynomials. This calculation quickly becomes complicated, and for the molecules of interest to us, multiple phonon emission is rare.) From the vibrational states given in Eq. (13), we are interested in the integral

$$O_{0,z} = \int dy \Psi_0^{(1)*} (y) \Psi_{2,a}^{(2)} (y - \Delta),$$  \hspace{0.5cm} (A1)

where we can split the integral into two parts:

$$= \int dy N_1 N_2 \sqrt{\frac{\omega_a}{\hbar}} \left[ \frac{\sqrt{2}}{\hbar} \right] \int dy \left[ e_2^{(2)} \cdot (y - \Delta) \right] e^{-(1/2h)(y^2/\Omega_{2a})}$$

$$\times e^{-(1/2h)(y^2/\Omega_{2a})} \{ (y - \Delta) \} e^{-(1/2h)(y^2/\Omega_{2a})}.$$  \hspace{0.5cm} (A2)

We want to make this expression look like the known Gaussian integral: $C_1 \int dx e^{-x^2} + C_2$ where $C_1$ and $C_2$ are constants. Changing the variables to $\tilde{y}$,

$$\tilde{y} = y - \Delta,$$

$$d\tilde{y} = dy,$$

we rewrite the integral as one over $d\tilde{y}$:

$$N_1 N_2 \sqrt{\frac{\omega_a}{\hbar}} \left[ \frac{\sqrt{2}}{\hbar} \right] \int d\tilde{y} \left[ e_2^{(2)} \cdot \tilde{y} \right] e^{-(1/h)(\tilde{y}^2/\Omega_{2a})}$$

$$\times e^{-(1/2h)(\tilde{y}^2/\Omega_{2a})}.$$  \hspace{0.5cm} (A3)

Expression (A3) is just $-\frac{1}{\sqrt{\pi}} \tilde{y} O_{0,0}$; we concentrate on expression (A2). First, as we did for the $O_{0,1}$ case, we rewrite this integral in terms of the quantities $\tilde{\Delta}$ and $\tilde{\Omega}$:

$$N_1 N_2 \sqrt{\frac{\omega_a}{\hbar}} \left[ \frac{\sqrt{2}}{\hbar} \right] \int d\tilde{y} \left[ e_2^{(2)} \cdot \tilde{y} \right] e^{-(1/h)(\tilde{y}^2/\tilde{\Omega}(y - \tilde{\Delta}))}$$

$$\times e^{-(1/2h)(\tilde{\Delta}) \Omega_{2a} e^{(1/2h)(\tilde{\Delta}) \Omega_{2a}}}.$$  \hspace{0.5cm} (A4)

We want to transform this integral into the appropriate normal-mode basis. We transform this integral into the appropriate normal-mode basis. Since we are integrating over the coordinates centered on $\tilde{\Delta}$ for a system with a Hessian of $\tilde{\Omega}$, we want to rewrite everything in terms of the eigenmodes of the averaged $\tilde{\Omega}$. We will call these eigenmodes $\tilde{\rho}_\beta$ where the following definitions hold

$$\tilde{y} = \sum_\beta p_\beta \tilde{\rho}_\beta,$$

$$\tilde{\Omega} \tilde{\rho}_\beta = \tilde{\omega}_\beta \tilde{\rho}_\beta.$$  \hspace{0.5cm} (A5)

Here, $\tilde{\rho}_\beta$ are the orthonormal eigenvectors for $\tilde{\Omega}$ and $\tilde{p}_\beta$ are the weights of each mode’s contribution to $\tilde{y}$. Hence,

$$\left( e_2^{(2)} \cdot \tilde{y} \right)^2 = \left( \sum_\beta p_\beta e_2^{(2)} \cdot \tilde{\rho}_\beta \right)^2 = \sum_\beta p_\beta^2 \left( e_2^{(2)} \cdot \tilde{\rho}_\beta \right)^2$$

$$+ \sum_{\beta \neq \beta'} p_\beta p_{\beta'} (e_2^{(2)} \cdot \tilde{\rho}_\beta) (e_2^{(2)} \cdot \tilde{\rho}_{\beta'}).$$  \hspace{0.5cm} (A6)

Again, the second term is odd in the new integration variables $p_\beta$ and will be zero. Rewriting the integral in $d\tilde{p}$ and remembering that $\tilde{p}$ diagonalizes $\tilde{\Omega}$, the integral from Eqs. (A1) and (A6) becomes

$$\int d\tilde{p} \sum_\beta p_\beta^2 \left( e_2^{(2)} \cdot \tilde{\rho}_\beta \right)^2$$

$$\exp \left( -\frac{1}{\hbar} \sum_\beta p_\beta^2 \tilde{\omega}_\beta \right) \left[ e^{-(1/2h)(\tilde{\Delta}) \Omega_{2a} e^{(1/2h)(\tilde{\Delta}) \Omega_{2a}}} \right].$$  \hspace{0.5cm} (A7)

Evaluating the integral over $d\tilde{p}$, we find

$$N_1 N_2 \sqrt{\frac{\omega_a}{\hbar}} \left[ \frac{\sqrt{2}}{\hbar} \right] \int d\tilde{p} \sum_\beta p_\beta^2 \left( e_2^{(2)} \cdot \tilde{\rho}_\beta \right)^2$$

$$\exp \left( -\frac{1}{\hbar} \sum_\beta p_\beta^2 \tilde{\omega}_\beta \right) \left[ e^{-(1/2h)(\tilde{\Delta}) \Omega_{2a} e^{(1/2h)(\tilde{\Delta}) \Omega_{2a}}} \right].$$  \hspace{0.5cm} (A8)
But \( \int x^2 e^{-Ax^2} dx = \frac{\sqrt{\pi}}{2A^{3/2}} \int e^{-x^2} dx \), so

\[
\int d^Dp \exp \left( -\frac{1}{\hbar} \sum_{\beta} p^2_{\beta} \bar{\omega}_{\beta} \right) = \frac{1}{2\omega_0 \hbar} \sqrt{\frac{\pi \hbar}{\omega_0}} \frac{1}{\sqrt{1 + \frac{\pi \hbar}{\omega_0}}} = \frac{\hbar}{2\omega_0 N^2}.
\]

(A11)

Hence, the first term in Eq. (A7) from Eq. (A10) becomes

\[
N_1N_2 \left( \frac{\omega_0}{\hbar} \right) \sum_{\beta} \left( \epsilon^{(2)}_\alpha \cdot \hat{\rho}_\beta \right)^2 \frac{\hbar}{2\omega_0 N^2} e^{(1/\hbar)\Delta^2} e^{-(1/2\hbar)\Delta^2} \Delta,
\]

which from Eq. (20) we see is

\[
O_{0,0} \left( \frac{\omega_0}{\hbar} \right) \sum_{\beta} \left( \epsilon^{(2)}_\alpha \cdot \hat{\rho}_\beta \right)^2.
\]

(A12)

Combining this with the third term from Eq. (A7) and expression (A3), our expression for the 0 → 2 overlap becomes

\[
O_{0,2 \to 0,0} = O_{0,0} \left\{ \sqrt{2} \omega_0 \sum_{\beta} \frac{1}{2\omega_0} \left( \epsilon^{(2)}_\alpha \cdot \hat{\rho}_\beta \right)^2 + \sqrt{2} \left( \frac{\omega_0}{\hbar} \right) \left( \epsilon^{(2)}_\alpha \cdot (\Delta - \Delta') \right)^2 - \frac{1}{\sqrt{2}} \right\}
\]

\[
= O_{0,0} \left\{ \frac{1}{2\omega_0} \left( \omega_0 \epsilon^{(2)}_\alpha \cdot \left( \hat{\rho}_\beta \hat{\rho}_\beta \right)^2 + \frac{1}{\hbar} \omega_0 \left( \epsilon^{(2)}_\alpha \cdot (\Delta - \Delta') \right)^2 - \frac{1}{\sqrt{2}} \right\}.
\]

(A14)

If \( \Omega_1 = \Omega_2 \) (i.e., there is no change in the harmonic potential), \( \Omega = \Omega_2 \) and hence \( \epsilon^{(2)}_\alpha \cdot \hat{\rho}_\beta = \delta_{\alpha \beta} \) and \( \omega_0 = \omega_0 \). The first term reduces to \( \frac{1}{\sqrt{2}} \), and the last term. Therefore in this case

\[
\left| \frac{O_{0,2 \to 0,0}}{O_{0,0}} \right|^2 = 2 \left( \frac{\omega_0}{\hbar} \right)^2 \left( \epsilon^{(2)}_\alpha \cdot (\Delta - \Delta') \right)^4 = \frac{g_a^2}{2}.
\]

(A15)

The change in harmonic potential per causing the molecule allows for phonon emission even in the absence of a configurational shift. Therefore, even if \( \Delta = \Delta' = 0 \), phonons can be emitted both because of frequency shifts \( (\omega_{\alpha} \neq \omega_{\beta}) \) and because the normal modes change \( (\epsilon^{(2)}_{\alpha} \neq \epsilon^{(2)}_{\beta}) \).

The other overlaps could be performed in a similar way. The strategy is to write everything in terms of integrals of \( f dxx^2 e^{-x^2} \) by transforming to the basis of the averaged Gaussian with \( \bar{\Omega} \). The odd-powered integrals are eliminated and the even-powered terms remain.\(^{34-36}\)


\( ^{40} \) X. H. Qiu, G. V. Nazin, and W. Ho, Phys. Rev. Lett. 92, 206102 (2004).


\( ^{45} \) Franck was the first to suggest that an electronic transition can be accompanied by a vibrational excitation using classical arguments (Ref. 13). Condon later duplicated the argument using quantum mechanics and the Born-Oppenheimer approximation. (Ref. 14). According to Condon, the intensity of a particular transition can be determined by calculating the transition dipole moment. The electronic component can be factored out, leaving the square of the phonon overlap to modulate the total transition.


\( ^{54} \) B. J. LeRoy, S. G. Lemay, J. Kong, and C. Dekker, Nature (Lon-