Vibrational Excitation in Single-Molecule Transistors: Deviation from the Simple Franck—Condon Prediction

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Received June 29, 2008; Revised Manuscript Received July 23, 2008

ABSTRACT

We investigated the inner-sphere reorganization of ferrocene ([Cp]2Fe^+) and tris(2,2′-bipyridine) iron ([bpy]3Fe^+) in a single-molecule-transistor geometry. In ([Cp]2Fe^+)(n = 0 and 1), almost no vibrations were excited during single-electron transport, whereas in ([bpy]3Fe^+)(n = 1, 2, and 3), many distinct vibrations appeared, consistent with its larger reorganization energy. The observed excitation intensities varied significantly across devices, however, and could not be accounted for by “Franck—Condon” factors. This observation indicates that a quantitative account of electron—vibration coupling in single-electron tunneling requires further investigation.

During reduction or oxidation, a molecule can undergo inner-sphere reorganization, a process in which the molecule geometrically distorts in order to accommodate the new charge state. Consequently, several vibrational states can be excited as an electron is added to or subtracted from the molecule, reminiscent of Franck—Condon processes where a vibrational excitation accompanies an electronic transition. Inner-sphere reorganization plays an important role in determining the charge transfer kinetics of molecules and is an essential element of the celebrated Marcus theory.1

The detailed experimental probing of inner-sphere reorganization requires a technique that allows for precise control over the number of electrons on the molecule while simultaneously recording vibrational states that couple strongly to the charging event. Single molecule transistors offer a unique opportunity to accomplish this: in a single-molecule transistor, an individual molecule is trapped between two metallic electrodes that act as source and drain, and the state charge of the molecule can be controlled using a capacitively coupled gate electrode.2—10 Recently, there has been considerable research activity in improving and expanding single-molecule electrical transport measurements, including the development of mechanically adjustable break junctions,7 ferromagnetic electrodes,6 and simultaneous laser spectroscopic measurements.8

Here, we report the vibrational-state-resolved investigation of inner-sphere reorganization in two transition-metal complexes, ([Cp]2Fe and ([bpy]3Fe, using the single-molecule-transistor technique. These molecules are chosen because they have been extensively studied as model systems, and they are stable in air and light. For both molecules, an abundance of IR and Raman spectroscopic data are available,11—14 and several electronic structure calculations have been performed on these species.15,16 The inner-sphere reorganization energy (a quantitative indicator of the vibrational excitations during an electron transfer event) of ([Cp]2Fe is known to be small (<0.03 eV).17,18 There have been fewer studies of the reorganization energy of ([bpy]3Fe. Although some studies have suggested that the ([bpy]3Fe reorganization energy can also be small,19,20 spectroscopic studies have shown that a significant geometrical distortion of ([bpy]3Fe occurs upon oxidation or reduction because of a pseudo-Jahn—Teller effect.21,22

Single-molecule transistors were prepared by depositing 5 or 6 drops of dilute submillimolar solutions of ([Cp]2Fe (in acetonitrile) or ([bpy]3Fe(ClO4)2 (in methanol) onto a 90 nm wide, 12 nm thick gold wire fabricated using electron-beam lithography. The break junction technique was then used to create a gap in the wire by electromigration.4,23 The gap size so generated was typically on the order of a few nanometers. The gold wire was fabricated on top of an aluminum pad with a ~3 nm native oxide layer that was used as a gate electrode. To minimize the probability that multiple molecules bridged the gap, the solution concentration was adjusted so that only ~10% of the junctions showed current—voltage characteristics different from an empty tunnel junction. Transport measurements of single-molecule transistors were performed at 300 mK or 1.5 K.
Figure 1 shows ball-and-stick models of the two molecules under interrogation, as well as representative current-voltage (I-V) curves taken at different gate voltages ($V_g$) from a single-(Cp)$_2$Fe transistor. As clearly seen in Figure 1b, the current is suppressed near zero bias and evolves in step-like jumps as the voltage is ramped. The size of the conductance region changes with $V_g$. These features are signatures of Coulomb blockade$^{2-4,24}$ and provide evidence that a single nanometer-sized object is responsible for the device behavior.

Figure 2 shows representative plots of differential conductance ($\partial I/\partial V$) as a function of $V$ and $V_g$ obtained from single-(Cp)$_2$Fe and (bpy)$_3$Fe transistors. Each device exhibits two conductance-gap regions bounded by two $\partial I/\partial V$ peaks that evolve linearly with $V_g$. At the intersection of these lines is the charge degeneracy point ($V_g = V_c$), where the two charge states are equivalent in energy, and the conductance gap vanishes. Within the conductance gap region, the charge state of the molecule is well-defined. In the regions outside of the conductance gap, electrons can tunnel on and off the molecule one electron at a time, and the molecular charge state fluctuates.

Because of the variable and poorly defined electrostatic environment between two electrodes, the molecule can acquire different charge states after deposition. The charge state of the molecule can be determined by performing the transport measurement under a magnetic field ($B$).$^{25}$ When an electron is added to the molecule, the total spin ($S$) of the molecule and thus the relative stability of successive charge states change under the $B$ field. This change results in a shift in $V_c$ ($\Delta V_c$) given by $\Delta V_c = -2g\mu_B\Delta S C_{tot}/C_g$, where $g$, $\mu$, $\Delta S$, $C_{tot}$, and $C_g$ represent the electron $g$ factor, the Bohr magneton, the spin change, the total capacitance, and the gate capacitance, respectively. In a similar fashion, the $\partial I/\partial V$ peaks bounding the conductance-gap regions split under $B$, exhibiting a characteristic Zeeman splitting pattern depending on $\Delta S$.$^{3,4}$ These $B$-field-dependent behaviors, coupled with the known $S$ values for each charge state of a molecule, allow for unambiguous charge state determination of the (Cp)$_2$Fe and (bpy)$_3$Fe species responsible for conduction.

Specifically, the data in Figure 3a show that the charge states responsible for conduction in the single-(Cp)$_2$Fe transistor are (Cp)$_2$Fe$^{1+}$ ($S = 1/2$) and (Cp)$_2$Fe$^0$ ($S = 0$) (more than 15 devices exhibited the same behavior). In the case of (bpy)$_3$Fe, on the other hand, both the (bpy)$_3$Fe$^{3+}$ ($S = 1/2$) and the (bpy)$_3$Fe$^{2+}$ ($S = 0$) states were observed. Of 11 devices studied, 5 showed evidence of the (bpy)$_3$Fe$^{3+}/$(bpy)$_3$Fe$^{2+}$ redox couple.
state to generate the \(+(n - 1)\) charged molecule in the ground or excited states. The energy of the quantized excitations can be determined from the bias voltage at which the \(\partial I/\partial V\) peaks intercept the border of the Coulomb blockade region.

Previous studies have shown that the electronically excited states of the \((\text{Cp})_2\text{Fe}^{n+}\) and \((\text{bpy})_3\text{Fe}^{n+}\) molecules lie at least 0.3 eV above the electronic ground state of these molecules.\(^{15,26}\) We therefore assign the \(\partial I/\partial V\) peaks observed in our single-molecule transistors (all with energies less than 0.2 eV) to vibrationally excited states of the molecule. Specifically, in the case of \((\text{Cp})_2\text{Fe}^{n+}\) (Figure 2a and Figure 3a), most devices showed the complete absence of vibrational excitations with energies exceeding 10 meV, whereas a few evenly spaced \(\partial I/\partial V\) features were observed with 0.3 and 3 meV spacings. The 0.3 meV excitation is so low in energy that it cannot correspond to an intramolecular vibration.\(^{14,27}\)

Instead, this excitation is most likely due to the center-of-mass oscillation mentioned above. The reason why this particular vibrational mode of \((\text{Cp})_2\text{Fe}\) is excited in the single-molecule-transistor geometry is not clear, but it might be due to mechanical coupling to the center-of-mass oscillation mentioned above.

Table 1. Summary of Peaks Observed in Eleven Single-(bpy)_3Fe Transistors, with Energies in Millielectronvolts along with Corresponding Mode Assignments from Previous Work in IR and Raman Spectroscopy\(^{11,12a}\)

<table>
<thead>
<tr>
<th>observed peak, oxidation (meV)</th>
<th>observed peak, reduction (meV)</th>
<th>IR/Raman peak (meV)</th>
<th>mode assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4 ± 0.65</td>
<td>9.3 ± 1.35</td>
<td>10.4</td>
<td>(\delta) (NMN)</td>
</tr>
<tr>
<td>15 ± 2.2</td>
<td>17.2 ± 0.9</td>
<td>18.8</td>
<td>(\delta) (NMN)</td>
</tr>
<tr>
<td>27.8 ± 2.05</td>
<td>26.4 ± 2.2</td>
<td>25.8</td>
<td>(\nu) (MN), (\delta) (NMN)</td>
</tr>
<tr>
<td>32.9 ± 1.5</td>
<td>31.1</td>
<td>16(^{b}) (\gamma) (ring)</td>
<td></td>
</tr>
<tr>
<td>38.4 ± 4.3</td>
<td>34.7 ± 2.2</td>
<td>35</td>
<td>(\nu) (MN) + comb</td>
</tr>
<tr>
<td>51.2 ± 1.5</td>
<td>49.3 ± 5.3</td>
<td>51.6</td>
<td>16(^{a}) (\gamma) (ring)</td>
</tr>
<tr>
<td>62.6 ± 2.35</td>
<td>60.1</td>
<td>comb</td>
<td></td>
</tr>
<tr>
<td>119.9 ± 1.85</td>
<td>119.5</td>
<td>128</td>
<td>5(^{b}) (\gamma) (C–H)</td>
</tr>
</tbody>
</table>

\(^{a}\) All peaks shown are vibrationally excited states of \((\text{bpy})_3\text{Fe}^{n+}\), excited during oxidation (observed in the \((\text{bpy})_3\text{Fe}^{n+}/(\text{bpy})_3\text{Fe}^{n+}\) couple) or reduction (observed in the \((\text{bpy})_3\text{Fe}^{n+}/(\text{bpy})_3\text{Fe}^{n+}\) couple).

(\text{Figure 3b}), and 7 contained the \((\text{bpy})_3\text{Fe}^{n+}/(\text{bpy})_3\text{Fe}^{n+}\) redox couple (\text{Figure 3c}). Of over 1000 junctions measured for each molecule, we were able to assign charge state in \(~30\) devices listed above. Other devices showing conductance characteristics distinct from that of an empty junction (<10% of all junctions measured) were either weakly coupled to the gate or too noisy, thereby prohibiting the firm assignment of molecular charge state.

With this charge-state assignment at hand, we can now turn our attention to the \(\partial I/\partial V\) peaks outside the conductance gap. These \(\partial I/\partial V\) peaks appear when a new quantized excitation becomes energetically accessible, providing an electron-tunneling pathway between the molecule and gold electrodes. For example, each \(\partial I/\partial V\) peak on the \(V_g < V_c\) side signifies the opening of a new conduction channel where an electron hops on the \(+n\) charged molecule in its ground

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**Figure 3.** \(\partial I/\partial V–V–V_g\) plots at \(B = 8\)T showing Zeeman splitting of single- (a) \((\text{Cp})_2\text{Fe}^{n+}/(\text{Cp})_2\text{Fe}^{n}\), (b) \((\text{bpy})_3\text{Fe}^{n+}/(\text{bpy})_3\text{Fe}^{n}\), and (c) \((\text{bpy})_3\text{Fe}^{n+}/(\text{bpy})_3\text{Fe}^{n+}\) transistors. Inset: corresponding magnetic field dependence of the charge degeneracy point. The peak evolves left or right with magnetic field, depending on the change in spin state during the charging event. The slopes in each data set are different because of the different degree of gate coupling, \(C_{\text{tot}}/C_g\), in each device. \(C_{\text{tot}}/C_g\) was 0.014 in (a), 0.17 in (b), and 0.08 in (c).
in single-(bpy)$_3$Fe transistors where the intensities of excited states were found to vary significantly from device to device. Figure 4 shows the intensities normalized to the ground-state transition for all observed transitions in each device. The trend lines show clear variation among devices. For instance, the relative intensity of the 17 meV excitation associated with the reduction of (bpy)$_3$Fe$^{2+}$ (observed in the (bpy)$_3$Fe$^{2+}$/(bpy)$_3$Fe$^{1+}$ couple) with respect to the ground-to-ground-state transition varied from 0.25 to 2.8 across our devices, and the relative intensity of the 26 meV excitation associated with the reduction of (bpy)$_3$Fe$^{2+}$ varied from 0.6 to 1.7. Similar variations have been observed in previous studies of C$_{70}$ and C$_{140}$ and p-mercaptoaniline.

The simple Franck–Condon picture considers the molecule in isolation, and it is possible that the environment of the molecule in this device geometry has a significant effect on charge transport. Previous theoretical studies have proposed several mechanisms that might be responsible for the observed intensity fluctuations: these include the coupling to the bosonic bath (source and drain electrodes), electron–vibration interaction leading to enhancement or reduction of conductance, and bias voltage-dependent contributions to the tunneling rate. Some of these mechanisms have been confirmed by experimental data as well: recently, Tal et al. showed that depending on the transmission probability, an inelastic scattering process between the electron and the vibration can increase conductance, or a virtual phonon can be absorbed and re-emitted by the electron to reduce conductance.

All of these effects should be sensitively dependent on the contact between the electrodes and the molecule. Moreover, some are predicted to depend on the gap shape and size that dictate the electric-field distribution around the molecule. Unfortunately, the electromigration-induced break-junction technique does not allow for the precise control over the contact properties or the field distribution. To illustrate this point, two representative devices in which the relative intensities of the 17 meV excitation associated with the reduction of (bpy)$_3$Fe$^{2+}$ vary from 0.24 (device 1) to 1.1 (device 2) were analyzed using a standard Coulomb-blockade model. From the slopes of the Coulomb diamonds and currents in each device, the capacitive and resistive coupling to each lead can be determined: in device 1 (2), the capacitance ratios with respect to source and drain leads are $C_D/C_S = 3$ ($33$) and $C_D/C_S = 4$ ($83$), and the source and drain resistances are $R_S = 1.59$ MΩ ($2.38$ MΩ) and $R_D = 140$ kΩ ($70$ MΩ). Across all devices measured, $C_D/C_S$ ranged from 0.4 to 2.5, and $R_S$ and $R_D$ varied from 10 kΩ to 100 MΩ. It is possible, therefore, that the variation in relative excited-state intensity is related to the variation in coupling to the leads, which in turn originates from differences among devices in molecular orientation and gap size. Unfortunately, the transport data presented here are not complete enough to discriminate between different theoretical models, and further systematic studies (for instance, using mechanically controlled break junctions where the molecule–electrode coupling can be better controlled) will be necessary to address this issue more clearly.
The single molecule transistor technique was used to study inner-sphere reorganization in two transition metal complexes, (Cp)2Fe and (bpy)3Fe. Qualitative differences in the inner-sphere reorganization energy of (Cp)2Fe; however, intensity variations among devices cannot be explained by the simple picture based on Franck-Condon factors alone, clearly illustrating that further theoretical and experimental studies are needed to address this intensity variation.

Acknowledgment. We thank J. R. Long, A. Falk, F. Koppens, B. Saar, S. Brittain, M. Wegewijs, H. Schoeller, E. Heller, and A. Aspuru-Guzik for useful suggestions and discussions. This work was supported by NSF and NDSEG.

References