NANO
LETTERS

2007
Vol. 7, No. 5
1364−1368

Vibronic Coupling in Semifluorinated Alkanethiol Junctions: Implications for Selection Rules in Inelastic Electron Tunneling Spectroscopy

**Jeremy M. Beebe,[†,‡] H. Justin Moore,[§] T. Randall Lee,[§] and
James G. Kushmerick*,[‡]**

*National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and
Department of Chemistry, University of Houston, Houston, Texas 77204-5003*

Received February 26, 2007; Revised Manuscript Received March 26, 2007

ABSTRACT

Determining the selection rules for the interaction of tunneling charge carriers with molecular vibrational modes is important for a complete understanding of charge transport in molecular electronic junctions. Here, we report the low-temperature charge transport characteristics for junctions formed from hexadecanethiol molecules having varying degrees of fluorination. Our results demonstrate that C–F vibrations are not observed in inelastic electron tunneling spectroscopy (IETS). Because C–F vibrations are almost purely dipole transitions, the insensitivity to fluorine substitution implies that Raman modes are preferred over infrared modes. Further, the lack of attenuation of the C–H vibrational modes with fluorine substitution suggests that either the scattering cross section is not an additive quantity or the physical position of a vibrational mode within the junction influences whether the transition is observed in IETS.

Inelastic electron tunneling spectroscopy (IETS) has recently become an important tool for characterizing metal−molecule−metal junctions, which are being examined as potential molecular electronic systems.[1−6] Though this technique has been in existence for over 40 years,[7] the fundamental physics regarding the manner in which the tunneling charge carrier interacts with a molecular vibration is still unclear. It is commonly believed that both infrared (dipole) and Raman (polarizability) modes are observed in IETS.[8] A variety of experiments[2,8] and calculations[9,10] also suggest that vibrational modes that occur along the direction of travel—longitudinal modes—have the largest scattering cross section. However, only a remarkably limited set of molecules has been examined using IETS, and thus neither of these concepts has been unambiguously demonstrated.

In optical techniques such as infrared (IR) spectroscopy, the molar absorptivity of a given vibrational mode is commonly determined. In contrast, there have been no systematic studies focused on quantifying the IETS scattering cross section, for example, by varying the number of a given bond type across a molecular series. The experiments presented in this letter have been designed to provide further insight into the types of vibrational modes present in tunneling spectra and also to begin to understand their relative intensities. Beyond the structure−function relationships explored here, the results of these experiments should prove useful for testing the various theoretical approaches to determining current−voltage ($I-V$) characteristics in molecular junctions.

Several theoretical approaches have recently been employed in an attempt to reproduce experimentally observed IET spectra.[11−15] Because there remains no standard theoretical approach to explain the $I-V$ behavior of molecular junctions, each of these groups arrives at a different result. One of the goals of the work presented herein is to provide the theoretical community with a robust data set that shows how specific changes in molecular structure influence observed IET spectra so that the validity of various theoretical models can be tested.

The experiments herein were designed specifically to determine how the IET spectrum changes when the quantity of a specific vibrational mode is changed. Through careful experimental design, we have examined a series of molecules in which the length of the molecular backbone remains constant while the number of fluorine atoms is varied (Figure 1). Our hypothesis was that if IETS intensity is additive, then by keeping the molecular length constant and varying the concentration of C−F versus C−H bonds in the molecule,

---

* Corresponding author. E-mail: james.kushmerick@nist.gov.

[†] Current address: Dow Corning Corporation, Midland, MI 48686.

[‡] National Institute of Standards and Technology.

[§] Department of Chemistry, University of Houston.

10.1021/nl070460r CCC: $37.00

F0 $CH_3(CH_2)_{15}SH$
F1 $CF_3(CH_2)_{15}SH$
F2 $CF_3CF_2(CH_2)_{14}SH$
F3 $CF_3(CF_2)_2(CH_2)_{13}SH$
F10 $CF_3(CF_2)_9(CH_2)_6SH$

Figure 1. Chemical structures of the molecules used in this study. The chain length of all molecules consists of 16 carbon atoms. Our adopted nomenclature is **FX**, where **X** denotes the number of fluorinated carbon atoms in the molecule.

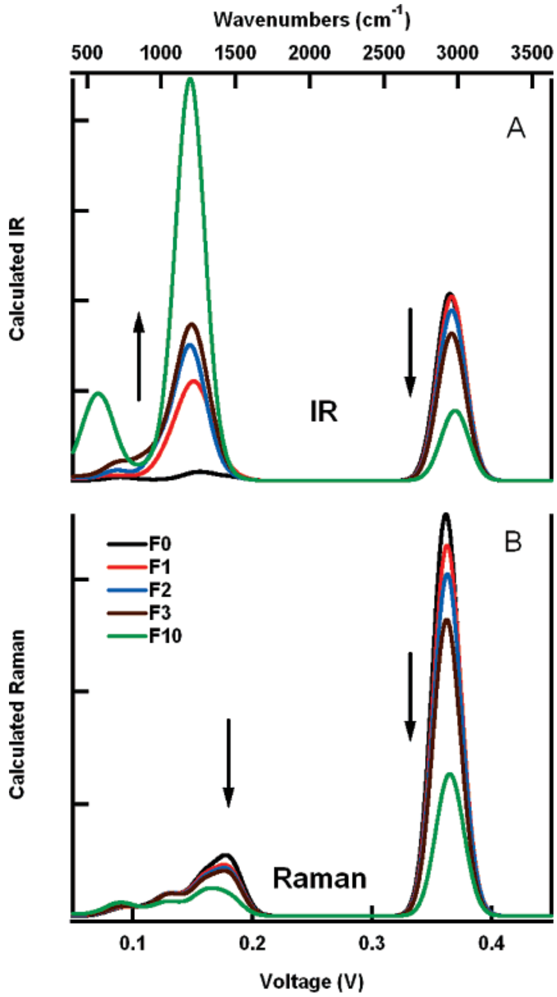

Figure 2. Calculated IR and Raman spectra for each of the molecules investigated. All spectra have been broadened with a Gaussian line shape to simulate the instrumental broadening of an IET spectrum. The arrows show how specific vibrational modes are affected as the molecules become more fluorinated. The spectra were calculated for free molecules at the B3LYP/6-31G* level of density functional theory, and the vibrational frequencies were scaled by a factor of 0.961.

it should be possible to determine an effective scattering cross section for both C−F and C−H vibrational modes.

Table 1. Tentative Assignments for the Observed Molecular Vibrations

observed peak position		calculated peak position		
mV	cm^{-1}	mV	cm^{-1}	mode
94	757	88	710	υ(C−S)
135	1086	128	1030	υ(C−C)
		136	1092	υ(C−C)
173	1394	160	1287	C−H wag
		181	1460	C−H scissor
359	2897	362−365	2920−2942	υ(C−H)

This concept is directly illustrated by the calculated gas-phase IR spectra for each of the molecules examined in this study (Figure 2A). As the number of fluorinated carbons increases from **F0** to **F10**, the calculated IR spectra show a growth of peaks at 1194 cm^{-1} (a combination of several C−F stretching modes) and 575 cm^{-1} (a combination of several C−F bending modes) and a corresponding decrease in intensity of the C−H stretching modes at ∼2900 cm^{-1}. In each spectrum, the peaks have been broadened with Gaussian line shapes to simulate the instrumental broadening that would occur if these same vibrations were observed by IETS (see within). The calculated IR spectra provide an excellent example of the behavior we would expect to observe if IETS intensity is an additive quantity. The molecular length is constant across the series, and the relative concentrations of C−F bonds and C−H bonds are systematically varied. In the calculated IR spectra, we observe an increase in the C−F peak intensities along with a corresponding decrease in the C−H peak amplitudes as the degree of fluorination increases. Therefore, if IR-active modes are observed in tunneling spectra, then the observed IETS signal should be sensitive to the number of fluorine atoms in the molecule.

In contrast, Figure 2B shows that the expected Raman response is remarkably similar for the entire series of molecules. Because of the amount of broadening necessary to simulate experimental IET spectra, the many individual vibrational modes present in the calculated spectra coalesce into four observed peaks at average positions of 757, 1086, 1394, and 2897 cm^{-1}. Assignments for the individual vibrational modes that contribute most strongly to each of these observed Raman peaks are compiled in Table 1. The polarizability change induced by a C−F stretching vibration is known to be small, and thus the shape of the calculated Raman spectrum does not change appreciably with increasing fluorine substitution. Therefore, if IETS is only sensitive to changes in polarizability, the shape of the observed spectra should be insensitive to fluorine substitution, although the peak magnitude of the C−H modes should decrease as more fluorine atoms are added to the molecule.

To probe the inelastic response of each of the molecules, transport measurements were performed in a custom-built cryogenic crossed-wire tunnel junction that has been previously described.[2,6] We formed self-assembled monolayers of each molecule by placing 10 μm Au wires in a solution of the molecules in ethanol and allowed the assembly to occur overnight. The physical structure of the monolayers of these molecules on Au surfaces has been previously determined.[16,17] Metal−molecule−metal junctions were constructed by placing monolayer-containing wires in proximity to bare Au wires in a stainless steel vacuum chamber, which was then evacuated, refilled with He gas, and lowered into

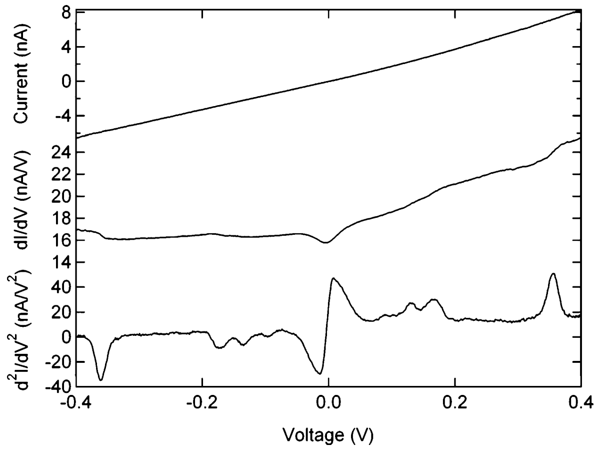

Figure 3. Transport characteristics for a Au/**F1**/Au junction. The first and second harmonic signals were obtained using an 8 mV RMS ac modulation amplitude and a lock-in time constant of 1 s.

a liquid He Dewar prior to obtaining current−voltage measurements. Junctions were completed by the Lorentz force generated between current flowing through the bare wire and a static magnetic field within the vacuum chamber. In a typical acquisition, voltage (±0.4 V) is swept at the top (bare) electrode while the bottom (monolayer-containing) electrode is held at ground and the current through the junction is measured. An additional ac voltage of 8 mV rms is coupled with the dc voltage sweep to enable measurement of the first and second harmonic signals (proportional to dI/dV and d^2I/dV^2,[2] respectively) with two lock-in amplifiers.

Figure 3 shows the transport properties for a Au/**F1**/Au junction. Although the $I-V$ traces in all IETS measurements are typically linear, the differential conductance (dI/dV) and IETS signal (d^2I/dV^2) exhibit significant features. One standard characteristic of all our IET spectra is the large feature at zero bias, commonly referred to as the zero-bias anomaly. Though the zero-bias anomaly is commonly attributed to phonon scattering in the metal leads, there remains some debate regarding its origin.[18,19] From repeated experiments utilizing decanethiol monolayers (data not shown), we have observed the magnitude and shape of the zero-bias feature to change significantly from one junction formation to the next, while the rest of the IET spectrum remains fairly constant. Because the details of the zero-bias feature do not appear to depend on the identity of the molecule in the junction, we choose to ignore this feature in our current analysis. As shown in Figure 3, the d^2I/dV^2 signal intensity is almost totally symmetric with respect to bias polarity. Therefore, for clarity, we show only the positive half of the total IET spectrum in subsequent figures.

Because the magnitude of the IETS signal depends directly on the total current through the junction, the spectra are normalized to account for differences in junction area from device to device. This normalization simply involves dividing d^2I/dV^2 by the differential conductance (dI/dV) of each junction and gives rise to a spectrum with intensity units of V^{-1}. The IET spectra of the semifluorinated hexadecanethiols are compiled in Figure 4. The amplitude of the observed peaks is similar for all molecules, suggesting that the spectra are fairly insensitive to fluorine substitution. Although there is a noticeable red-shift of the two lowest energy vibrations of the **F10** junction, it is clear that the main spectral features arise from the same vibrations for each molecule across the series.

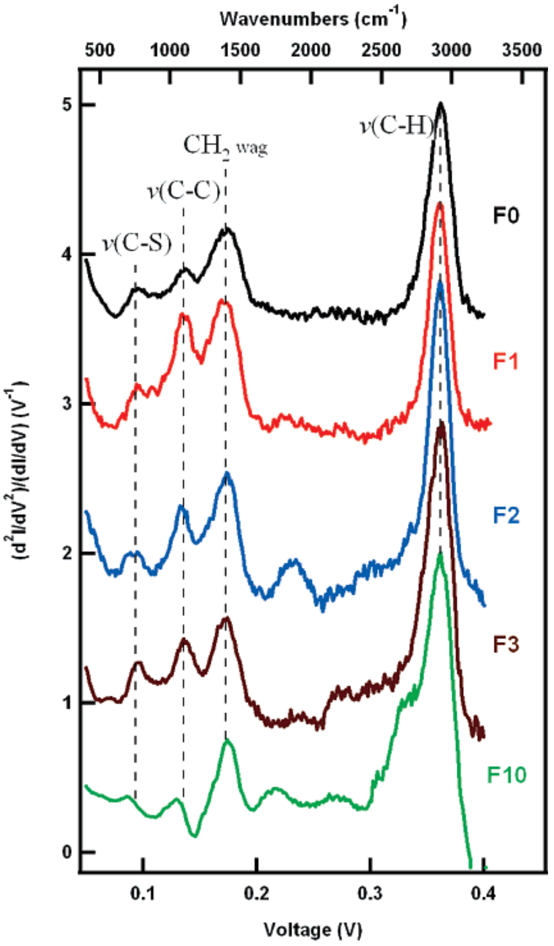

Figure 4. Tunneling spectra of each of the five molecules examined in this study. All spectra share a common vertical scale and have been offset for clarity. The dashed vertical lines represent the average position of each peak.

To determine the sensitivity limitations inherent in our junction formation technique, we formed five separate Au/decanethiol/Au junctions and determined the variance in the amplitudes (data not shown). The results of this control experiment showed that the junction-to-junction variance in peak area for the ν(C−H) mode is greater than 20%, and thus the IET spectra of all of the semifluorinated molecules are indistinguishable within our measurement uncertainty. Two interesting observations can be made from these results: (1) There are more C−F bonds than C−H bonds in the **F10** molecule, but the **F10** spectrum and the **F0** spectrum are essentially identical. Therefore, it appears that *tunneling charge carriers do not couple to C−F νibrations*. (2) There is no significant loss of signal intensity for the C−H stretching mode (or any of the observed IETS modes) across the entire series upon fluorine substitution. Therefore, *the C−H peak amplitude does not depend appreciably on the number of C−H bonds in the molecule.* Interestingly, the peak most strongly affected by the F substitution is the

ν(C−C), which likely is a result of structural changes for the carbon backbone in the **F10** monolayer.[16] From comparison of the measured IET spectra with the calculated gas-phase Raman and IR spectra, it is clear that IET spectra are well described by the calculated Raman spectra and decidedly at odds with the calculated IR spectra.

The relative intensity of calculated vibrational modes for IET spectra depends strongly on the theoretical framework. Early theoretical models of IETS differed in which type of vibrational mode would be most strongly observed. Modeling the electron−phonon coupling as a perturbation to the barrier height predicts that infrared modes should be 1−10 times as intense as Raman modes.[20,21] In contrast, a transfer-Hamiltonian formalism predicted that Raman and infrared mode intensities should be roughly equal.[22] Previous experiments designed to address this issue were hampered by the fact that the chosen molecules did not possess sufficient symmetry to unequivocally separate the two types of modes, and therefore it is possible that peaks that were assigned as IR in character actually arose from the minor Raman contributions to a given mode.[8] Here, we have examined C−F vibrations, which are known to have large dipole transitions but only small changes in bond polarizability. The calculated Raman spectra of these molecules clearly show that C−F modes are not Raman-active, regardless of the number of these modes present in the molecule. The absence of these modes in the IET spectra of the semifluorinated alkanethiol series is certainly consistent with a preference toward the observation of Raman modes over IR modes in IETS.

It is important to note that it is not yet obvious whether the apparent *invisibility* of the C−F modes truly indicates that IET spectra are insensitive to IR modes or whether some combination of other factors is responsible for the absence of observed C−F peaks. The potentially more important observation in this study is that the ν(C−H) peak amplitude is constant across the molecular series, even though the number of C−H bonds is changed by over 50%. One potential explanation for this behavior is that IETS is sensitive only to the presence or absence of a particular vibrational mode within the transport pathway. To state it another way, the scattering cross section is not an additive quantity. In effect, this scenario would mean that the matrix element for coupling the tunneling electron to C−H modes is large regardless of the number of C−H modes present.

A second possibility is the existence of a *proximity effect*, that is, the position of a vibration within a molecule (or more specifically within a molecular junction) determines whether it is observed. In this specific case, we have substituted fluorine atoms for hydrogen atoms at the molecular terminus far away from the S−Au bond. The metal−molecule coupling at the chemically bound contact should be much greater than at the physical metal−molecule contact,[23,24] and therefore it is possible that the strongest coupling will be observed for vibrations occurring near the S−metal contact. Although the exact method by which the S−metal contact would *activate* the vibrational modes is unclear, recent theoretical work has shown that the pathway taken by the tunneling electron can affect the IET spectrum.[10] Another complication with this analysis is that the IETS peak amplitudes are symmetric with respect to bias polarity, which means that the coupling strength of tunneling electrons to the observed vibrational modes is the same whether the charge is injected at the chemically bound or physically placed contact. Nonetheless, the observed spectra are definitely insensitive to atomic substitution far from the S−Au contact, which supports the idea of a proximity effect.

This molecular series also sheds light on another aspect of IETS propensity rules. Recent numerical calculations aimed at interpreting the observed IET spectra of alkanethiol monolayers on gold[2,3] predicted only a small ν(C−H) peak amplitude.[11,13,14] It was postulated that the intensity difference between the calculated spectra (obtained for alkane-dithiols) and the observed undecanethiol spectrum could be explained by the presence of CH_3 vibrational modes, which are absent in the dithiol.[11,14] Although the only molecule in the semifluorinated series that is methyl-terminated is **F0**, Figure 4 clearly shows that the C−H stretch dominates the IET spectrum for each of the five molecules examined. Therefore, the intensity of the C−H stretching mode does not arise solely from CH_3 vibrations.

In summary, we have measured the IETS response of a systematic series of semifluorinated alkanethiol monolayers self-assembled on gold. We have observed these spectra to be insensitive to the degree of fluorine substitution, which raises questions regarding the factors that influence the scattering cross section for a given vibrational resonance. These results should be excellent benchmarks for theoretical comparison and should thus provide a pathway toward better understanding of the factors that govern charge transport in molecular electronic junctions.

Acknowledgment. We acknowledge support from the Defense Advanced Research Project Agency (J.M.B. and J.G.K.) as well as the National Science Foundation (DMR-0447588) and the Robert A. Welch Foundation (E-1320) (H.J.M. and T.R.L.).

References

(1) Ho, W. *J. Chem. Phys.* **2002**, *117*, 11033−11061.
(2) Kushmerick, J. G.; Lazorcik, J.; Patterson, C. H.; Shashidhar, R.; Seferos, D. S.; Bazan, G. C. *Nano Lett.* **2004**, *4*, 639−642.
(3) Wang, W.; Lee, T.; Kretzschmar, I.; Reed, M. A. *Nano Lett.* **2004**, *4*, 643−646.
(4) Yu, L. H.; Keane, Z. K.; Ciszek, J. W.; Cheng, L.; Stewart, M. P.; Tour, J. M.; Natelson, D. *Phys. Rev. Lett.* **2004**, *93*, 266802.
(5) Selzer, Y.; Cai, L. T.; Cabassi, M. A.; Yao, Y. X.; Tour, J. M.; Mayer, T. S.; Allara, D. L. *Nano Lett.* **2005**, *5*, 61−65.
(6) Yu, L. H.; Zangmeister, C. D.; Kushmerick, J. G. *Nano Lett.* **2006**, *6*, 2515−2519.
(7) Jaklevic, R. C.; Lambe, J. *Phys. Rev. Lett.* **1966**, *17*, 1139−1140.
(8) Hansma, P. K., Ed., *Tunneling Spectroscopy: Capabilities, Applications, and New Techniques*. Plenum Press: New York, 1982.
(9) Chen, Y. C.; Zwolak, M.; Di Ventra, M. *Nano Lett.* **2004**, *4*, 1709−1712.
(10) Troisi, A.; Ratner, M. A. *Small* **2006**, *2*, 172−181.
(11) Troisi, A.; Ratner, M. A. *Phys. Rev. B* **2005**, *72*, 033408.
(12) Jiang, J.; Kula, M.; Luo, Y. *Nano Lett.* **2005**, *5*, 1551−1555.
(13) Solomon, G. C.; Gagliardi, A.; Pecchia, A.; Frauenheim, T.; Di Carlo, A.; Reimers, J. R.; Hush, N. S. *J. Chem. Phys.* **2006**, *124*, 094704.

(14) Paulsson, M.; Frederiksen, T.; Brandbyge, M. *Nano Lett.* **2006**, *6*, 258−262.
(15) Kula, M.; Jiang, J.; Luo, Y. *Nano Lett.* **2006**, *6*, 1693−1698.
(16) Weinstein, R. D.; Moriarty, J.; Cushnie, E.; Colorado, R.; Lee, T. R.; Patel, M.; Alesi, W. R.; Jennings, G. K. *J. Phys. Chem. B* **2003**, *107*, 11626−11632.
(17) Colorado, R.; Lee, T. R. *Langmuir* **2003**, *19*, 3288−3296.
(18) Weber, H. B.; Haussler, R.; von Lohneysen, H.; Kroha, J. *Phys. Rev. B* **2001**, 63.
(19) Gregory, S. *Phys. Rev. B* **1991**, *44*, 12868−12872.
(20) Lambe, J.; Jaklevic, R. C. *Phys. Rev.* **1967**, *165*, 821−832.
(21) Scalapino, D. J.; Marcus, S. M. *Phys. Rev. Lett.* **1967**, *18*, 459−461.
(22) Kirtley, J.; Scalapino, D. J.; Hansma, P. K. *Phys. Rev. B* **1976**, *14*, 3177−3184.
(23) Taylor, J.; Brandbyge, M.; Stokbro, K. *Phys. Rev. Lett.* **2002**, *89*, 138301.
(24) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. *Phys. Rev. Lett.* **2002**, *89*, 086802.

NL070460R