# Inelastic Electron Tunneling Spectroscopy of an Alkanethiol Self-Assembled Monolayer Using Scanning Tunneling Microscopy

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We report inelastic electron tunneling spectroscopy (IETS) of a $C_8$ alkanethiol self-assembled monolayer using a scanning tunneling microscope (STM). High-resolution STM IETS spectra show clear features of the C-H bending and C-C stretching modes in addition to the C-H stretching mode, which enables a precise comparison with previously reported vibrational spectroscopy, especially electron energy loss spectroscopy data. Intensity variation of vibrational peaks with tip position is discussed with the STM IETS detection mechanism.

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Intensive studies have been executed for the understanding of electron transport through a single molecule that bridges two metal electrodes [1–3]. These results have revealed intriguing electric phenomena, but the necessity of the characterization of molecules between electrodes has also been realized. Inelastic tunneling spectroscopy (IETS) is one of a few candidates for a chemical-analysis tool of molecules in a tunneling junction through a detection of vibrational modes of the molecules. We can see several IETS studies in which an alkanethiol molecule was employed as a standard molecule to characterize nanoscale electrodes. However, quite a large discrepancy of the IETS spectra has been reported when different types of electrodes were used [4–6]. To evaluate the electrodes, it is important to establish a "standard" IETS spectrum.

IETS measurement using a scanning tunneling microscope (STM) has been initiated a decade ago [7]. STM IETS can provide such standard spectra because we can characterize molecules by various techniques prior to a formation of a metal-molecule-metal junction. In addition, the contact can be tuned by changing the distance between a tip and a molecule. However the number of reports of STM IETS for the alkanethiol molecules is limited [8].

Here in this Letter, we show an STM IETS measurement of a $C_8$ alkanethiol self-assembled monolayer (SAM) using a cryostat STM at a temperature of 4.3 K. The measured STM IETS spectra have detected practically all vibrational modes measured by electron energy loss spectroscopy (EELS) [9,10]. To our knowledge, this is the first report in which vibrational features detected by the two techniques can be compared in a high precision manner. The tilt angle of the molecules has been changed by pushing the layer with the STM tip, and the intensities of some of the vibrational features show a variation that can be explained by a change of dipole moments with the tilt of the molecules.

A low temperature STM head (Unisoku Co. Ltd, Japan) is attached to a cold finger of a dilution refrigerator (Taiyo Nissan, Japan), which is housed in a vacuum chamber surrounded by a liquid He dewar. With the operation of a dilution cryostat, the sample can be cooled to the temperature of ~260 mK. However, the data shown here were taken at the sample temperature of 4.3 K. The STM was controlled with commercial electronics (RHK, USA). $\mathrm{d}I/\mathrm{d}V$ and $\mathrm{d}^2I/\mathrm{d}V^2$ are obtained simultaneously using the standard method with the use of the lock-in amplifier (LI5640, NF Corp., Japan), which has been described in previous papers [11]. The tip was placed on a bright spot in the STM image of a $C_8$ SAM. Though further lateral tracking of the tip position was not executed, the lateral drift of the tip position was limited and was less than a unit of the alkanethiol lattice for a day.

A SAM film of a $C_8$ alkanethiol molecule was prepared by immersing an Au(111)/mica sample into hexane solution of $C_8$ alkanethiol (1 m$M$) for 6 min, and rinsing with ethanol just before inserting into a vacuum chamber for STM observation. The Au/mica sample (MI, USA) was annealed in air using a hydrogen torch before immersing in

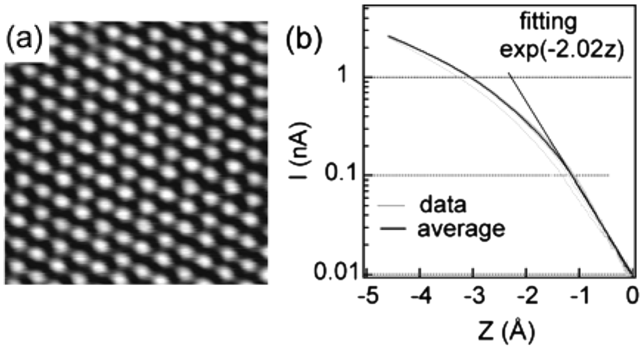

FIG. 1. (a) Topological STM image of $C_8$ alkanethiol molecules on Au(111) ($5.4 \times 5.4$ nm$^2$, $I_t = 83$ pA, and $V_s = -2.5$ V). (b) Variation of the tunnel current with tip movement ($I - z$ curve). The tip approached at a rate of $\approx 0.35$ Å/s from the position of $I_t = 0.1$ nA and $V_s = 500$ mV. The linear line is the result of least square fitting with a function of $I \sim \exp(-\alpha z)$.

the solution. As shown in Fig. 1(a), an ordered structure of the $C_8$ alkanethiol SAM with $\sqrt{3} \times \sqrt{3}$ R30° periodicity has been observed [12].

The gap between the tip and molecule has been examined by the $I - z$ curve shown in Fig. 1(b), which has been measured by moving the tip from the initial position ($z = 0$), that is defined by the conditions of $I_t = 10$ pA and $V_s = 500$ mV, to the substrate. The $I - z$ curve can be fit with a straight line at an initial stage of the approach ($z < -1.5$ Å), which can be expressed as $I \propto \exp(-\alpha z)$ with $\alpha = 2.02$ Å$^{-1}$. The constant $\alpha$ is comparable with the previous report of the vacuum barrier of $\alpha = 2.4$ Å$^{-1}$ [13]. After reaching $z = -1.5$ Å that gives $I_t = \sim 0.2$ nA at $V = 500$ mV, the curve shows a bend and is deviated from a straight line. The slope after the bend can be estimated as $I \propto \exp(-\beta z)$ with $\beta = 1.1$ Å$^{-1}$ at its initial stage, though $\beta$ becomes smaller with further approach of the tip. The decay rate of the tunneling current through a monolayer of $C_n$ alkanethiol SAM has been analyzed previously using various chain lengths of $n$ [14,15], and the decay in the molecular layer has been deduced to be $I \propto \exp(-\beta z)$ with $\beta = 1.2$ Å$^{-1}$ [15]. We consider that the tip and the SAM contact at $z = -1.5$ Å, and the decay length in the SAM layer is close to the value that has been reported for alkanethiol layers. The decay length becomes smaller with further approach of the tip, which we speculate is due to the conformational change of the molecule layer caused by the tip.

Figure 2(a) shows $dI/dV$ and $d^2I/dV^2$ vs $V$ obtained at 4.3 K on $C_8$ alkanethiol SAM. The spectra have been taken after positioning the tip at $I_t = 1$ nA and $V_s = 500$ mV, and the modulation voltage of $V_{\rm rms} = 7.2$ mV has been added to the bias voltage. The tip has approached beyond the contact point with the molecule layer according to the curve of Fig. 1(b). The $d^2I/dV^2 - V$ curve shows features that appear at symmetric energy positions about the Fermi level with a reversed polarity. This satisfies conditions required to assign them as vibrational features [7,16].

A prominent feature appears at the energy of ±361 mV. Features at similar energy have been reported in the STM IETS of hydrocarbon molecules like $C_2H_2$ on Cu(100) [7,17], and *cis* and *trans*-2-butene molecules on Pd(110) [18,19], which has been attributed to the C-H stretching mode ($\nu$(C-H)). In all reports, the $\nu$(C-H) feature dominates the IETS spectra and other vibrational features are less obvious. On the other hand, the spectrum of Fig. 2(a) shows clear peaks between 50 and 200 meV. They also satisfy the criteria for assigning them to be vibration modes, and the vibrational modes in this energy range include C-H bending modes and a C-C stretching mode. The change of the conductance ($\Delta\sigma/\sigma$) deduced from $dI/dV$ is ~3.0% for the C-H stretching mode (361 mV) and ~1.2% for $CH_3$ deformation (171 mV). The measured $\Delta\sigma/\sigma$ of the C-H stretching mode exceeds 10% for $C_2H_2$ [7]. Thus, the relative yield of C-H bending and C-C stretching modes in reference to C-H stretching mode is high in alkanethiol SAM.

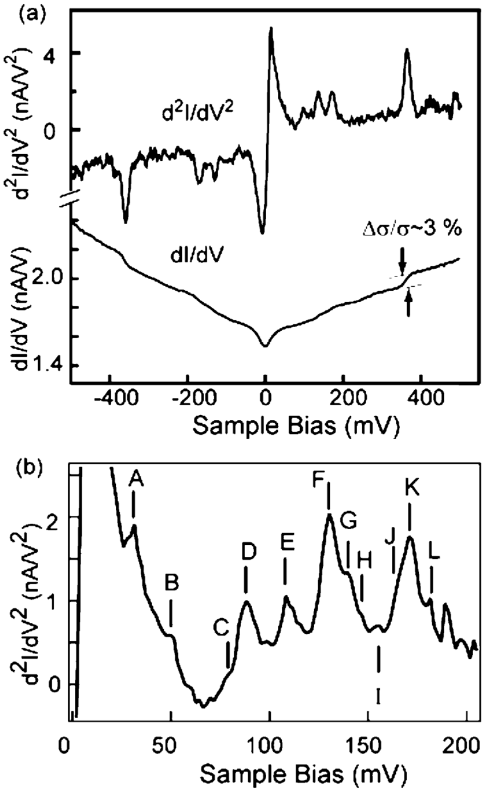

FIG. 2. (a) The plot of $dI/dV$ (lower) and $d^2I/dV^2$ (upper) vs $V$ on $C_8$ alkanethiol molecules on Au(111) at 4.3 K. The tip was positioned at $I_t = 1$ nA and $V_s = 500$ mV. The plot is an average of 32 cycles of the measurements, and it takes ~7 min for each cycle. (b) High-resolution STM IETS obtained with $V_{\rm mod} = 3.6$ mV and the set point of $I_t = 1$ nA at $V_s = 500$ mV. The marks at peaks correspond to the ones in Table I.

Here we consider the mechanism of higher yield for these modes in the current system. Theoretical discussion for the peak intensity of STM IETS features has been made for small molecules [20], and more recently for larger molecules [21]. These studies have emphasized that the coupling between electronic states of substrates and vibrational modes determines the strength of peaks. Higher yield of the modes between 50 and 200 meV detected in this experiment might be related to the upright bonding configuration of the alkanethiol molecule, which expectedly makes the interaction of substrate and molecule weaker. In phenomena like tunneling electron induced light emission from molecules [22] and the inelastic tunneling process of spin flip of an isolated spin [23], it has been observed that the yield of the signals has increased in case the bonding between molecules and substrates is weakened. We speculate that a similar situation is realized for STM IETS of $C_8$ SAM.

For further analysis of the vibrational modes, we show STM IETS spectra detected with higher resolutions. The peak width of STM IETS spectra is the convolution of the thermal broadening, the modulation voltage applied to the bias voltage, and the intrinsic peak width. The behavior should be expressed with the following formula:

$$W = \sqrt{\left(5.4\frac{kT}{e}\right)^2 + (1.7V_{\mathrm{mod}})^2 + W_1^2} \qquad (1)$$

where $k$ is the Boltzmann constant, $T$ is the temperature, $V_{\mathrm{mod}}$ is the modulation voltage (rms), and $W_1$ is an intrinsic width of the peak [8]. The results of our measurements of resolution vs modulation voltage for the C-H stretching mode (~361 mV) are well reproduced with this formula.

Figure 2(b) shows a high-resolution STM IETS spectrum obtained with the modulation voltage of $V_{\mathrm{rms}} = 3.6$ mV. The expected resolution from formula (1) is ~6 mV without considering the intrinsic peak width, which can be comparable with the one of EELS measurement. The set point was $I_t = 1$ nA and $V_s = 500$ mV. About 700 spectra were accumulated for averaging and each spectrum was taken in a period of 3 min, and special attentions have been paid to the reproducibility of the peaks. The energy positions of the detected vibrational features are compared with the result of the EELS measurement [9,10]. The comparison is summarized in Table I, in which the marks of the features correspond to the ones in Fig. 2(b). We consider that the agreement is good and all features measured by EELS techniques are reproduced by our current measurement.

Next, we show the variation of spectra with a change of the tip-sample distance. Further approach of the tip has changed the spectra shape, which is shown in Fig. 3. The set points are $I_t = 1$ nA, 2 nA, and 3 nA at 500 mV, and the modulation voltage is $V_{\mathrm{rms}} = 2.7$ mV. The vibration features of $A$–$K$ marked in Fig. 3 show no change in their energy positions with the variation of the tip position. This is also true for the C-H stretching mode, though it is not shown in this figure. However, the peak intensities of the features $A$–$K$ show intriguing changes. For example, with the increase of $I_t$, the relative intensity of the $CH_3$ deformation feature of $K$ and the $CH_2$ rock mode of $D$ has decreased, but that of the $CH_3$ rock mode of $E$ has increased.

TABLE I. Comparison of vibrational features of the current data and EELS data [10]. Omitted marks also have matching features.

| Peak | Mode | STM IETS (mV) | EELS (mV) |
|---|---|---|---|
| $A$ | Au-S stretch | 31 | 32 |
| $D$ | $CH_2$ rock | 88 | 89 |
| $E$ | $CH_3$ rock | 108 | 113 |
| $F$ | C-C stretch | 130 | 130 |
| $K$ | $CH_3$ $s$ deform | 171 | 172 |
| $L$ | $CH_2$ scissors, $CH_3$ $d$ deform | 182 | 180 |

We would like to compare the peak positions and intensity behavior with the ones of the previous EELS data [9,10], and a recent theoretical calculation [24]. The latter has been performed as an estimation of conductance through a $C_{11}$ alkanethiol molecule sandwiched by two Au surfaces, in which each vibrational mode increases the conductance for a bias above the vibrational energy.

The first interesting observation is the high peak intensity of the C-C stretching mode (feature $F$). This mode has been observed in Raman [25], infrared (IR) [26], and EELS measurements [9,10], but the relative peak intensity was weak in all of them. In the theoretical simulation, on the other hand, it has been calculated as the strongest vibrational feature [24]. This shows a good agreement with our observation. We speculate that the conducting electrons can couple with this mode strongly. The conductance can be estimated ~0.4–0.5 nA/V from Fig. 1(b) at the molecule-tip contact, which is comparable with the calculated value of 1.2 nA/V even though there is a chain length difference [24].

Next, we examine the feature $K$ at ~171 mV. A feature at almost the same energy has been observed by IR [26] and EELS [10], which has been assigned to a symmetric deformation mode of $CH_3$ group. Those reports have discussed that the intensity of this peak shows an alternative change with the chain length of $n$; a strong signal for even $n$ and a weak one for odd $n$. The intensity change has been attributed to the difference of the direction of the $CH_3$ group. A strong feature is observed for even $n$, because the variation of the dipole moment of this mode is surface normal.

A clear observation of this feature in Figs. 2(b) and 3 (feature $K$) indicates that the vibrational mode of $CH_3$ is

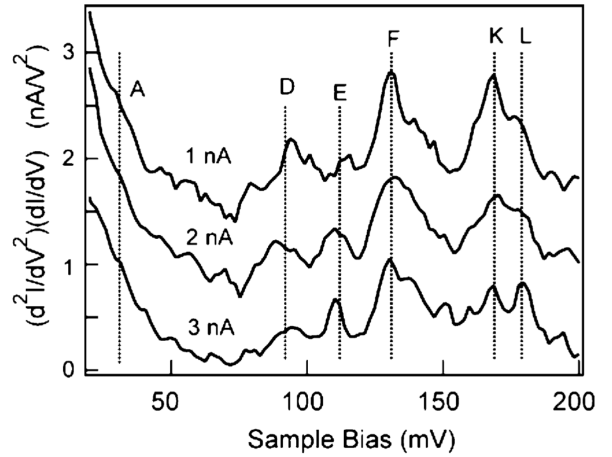

FIG. 3. Variation of the $d^2I/dV^2$ spectra with set points of 1 nA, 2 nA, and 5 nA at $V_s = 500$ mV are compared. A modulation voltage of $V_{\mathrm{rms}} = 2.7$ mV was applied. Vertical lines and legends are eye guides for the peak positions, and the legend marks correspond to the ones in Fig. 2(b) and Table I.

actually excited by the tunneling current. Judging from Fig. 1(b), the tip contacts the SAM film at $I_t = 0.2$ nA and $V_s = 500$ mV. Since the $CH_3$ symmetric deformation mode is clearly observed even when the tip approaches the film beyond the contact point, it is not likely that the tip is penetrated into the molecule layer and is placed below the $CH_3$ group. Instead, we consider that the tip is pushing the molecule and the alkanethiol molecule is further tilted from the surface normal direction.

The intensity of this mode ($K$) has decreased when the tip has been further approached to the set point of $I_t =$ 3 nA and $V_s = 500$ mV. The same process increases the intensity of the $CH_3$ rock mode (feature $E$). It is interesting to see that those two modes of $K$ and $E$ have a reversed odd-even effect in their intensities in the previous reports; the intensity of the $CH_3$ rock mode has increased for odd $n$ [10,26].

One possible explanation of this intensity variation can be deduced from the change of the tilt angle of the molecules by being pushed by the STM tip and the "dipole coupling" excitation mechanism of IETS. The mechanism has explained an observation in conventional IETS experiments that vibrational modes that are strongly infrared active give a strong signal in IETS [16,27,28]. By approaching the tip to the set point of $I_t = 3$ nA and $V_s =$ 500 mV, the top of the molecule layer is estimated to be pushed ~3 Å from the contact point, which increases the tilt angle of the $C_8$ molecule to ~48° from the initial value of ~26° [29].

The tilt angle change makes the odd-even phenomena less obvious. In this situation, a decrease of "even" feature $K$ and an increase of "odd" feature $E$ in intensity are expected with IR measurement. With the dipole coupling mechanism, a similar behavior is expected in STM IETS measurement, which agrees with the changes observed in Fig. 3. However, further theoretical calculations are required to understand how these structural configurations affect the intensity variation of IETS peaks.

Finally we would like to compare the current result with the IETS data obtained with cross-wire electrodes [4] and nanopore electrodes [5]. The IETS spectra measured by using cross-wire electrodes showed an extraordinary good agreement with our current data, both of the energy positions and the relative intensities of the peaks [4]. On the other hand, the comparison with the report of Wang shows little similarities [5]. A recent report by Yu *et al.* has demonstrated that the metal impurities among molecules can produce the peaks observed by Wang *et al.* [6]. We should consider that the cross-wire junction has offered less damage for the alkanethiol molecules in the junctions.

In summary, we have shown STM IETS measurement of $C_8$ alkanethiol SAM at 4.3 K. Practically all components of vibrational modes that have been detected using EELS in previous reports have been observed, which we believe is the first case in STM IETS observation. A variation of peak intensities of those modes with a change of the tilt angle of a $C_8$ molecule by being pushed by a STM tip has been detected for several modes. The behavior might be explained with a "dipole coupling" that has been discussed in conventional IETS to account for the phenomena that infrared-active vibrational-mode gives a strong signal in IETS.

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[1] L. A. Bumm *et al.*, Science **271**, 1705 (1996).
[2] M. A. Reed *et al.*, Science **278**, 252 (1997).
[3] J. G. Kushmerick *et al.*, Phys. Rev. Lett. **89**, 086802 (2002).
[4] J. G. Kushmerick *et al.*, Nano Lett. **4**, 639 (2004).
[5] W. Y. Wang *et al.*, Nano Lett. **4**, 643 (2004).
[6] L. H. Yu, C. D. Zangmeister, and J. G. Kushmerick, Phys. Rev. Lett. **98**, 206803 (2007).
[7] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **280**, 1732 (1998).
[8] A.-S. Hallback *et al.*, Nano Lett. **4**, 2393 (2004).
[9] G. J. Kluth, C. Carraro, and R. Maboudian, Phys. Rev. B **59**, R10449 (1999).
[10] H. S. Kato *et al.*, J. Phys. Chem. B **106**, 9655 (2002).
[11] Y. Sainoo *et al.*, J. Chem. Phys. **120**, 7249 (2004).
[12] G. E. Poirier, Langmuir **15**, 1167 (1999).
[13] U. Durig, J. K. Gimzewski, and D. W. Pohl, Phys. Rev. Lett. **57**, 2403 (1986).
[14] M. Salmeron *et al.*, Langmuir **9**, 3600 (1993).
[15] L. A. Bumm *et al.*, J. Phys. Chem. B **103**, 8122 (1999).
[16] P. K. Hansma, *Tunneling Spectroscopy* (Plenum Press, New York, 1982).
[17] B. C. Stipe, M. A. Rezaei, and W. Ho, Phys. Rev. Lett. **82**, 1724 (1999).
[18] Y. Kim, T. Komeda, and M. Kawai, Phys. Rev. Lett. **89**, 126104 (2002).
[19] Y. Sainoo *et al.*, Phys. Rev. Lett. **95**, 246102 (2005).
[20] N. Lorente *et al.*, Phys. Rev. Lett. **86**, 2593 (2001).
[21] J. B. Maddox *et al.*, J. Phys. Chem. A **110**, 6329 (2006).
[22] X. H. Qiu, G. V. Nazin, and W. Ho, Science **299**, 542 (2003).
[23] A. J. Heinrich *et al.*, Science **306**, 466 (2004).
[24] M. Paulsson, T. Frederiksen, and M. Brandbyge, Nano Lett. **6**, 258 (2006).
[25] M. A. Bryant and J. E. Pemberton, J. Am. Chem. Soc. **113**, 8284 (1991).
[26] R. G. Nuzzo, L. H. Dubois, and D. L. Allara, J. Am. Chem. Soc. **112**, 558 (1990).
[27] J. Kirtley and P. Soven, Phys. Rev. B **19**, 1812 (1979).
[28] K. W. Hipps and U. Mazur, J. Phys. Chem. **97**, 7803 (1993).
[29] P. E. Laibinis *et al.*, J. Am. Chem. Soc. **113**, 7152 (1991).