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Role of Molecular Orbitals Near the Fermi Level in the Excitation of Vibrational Modes of a Single Molecule at a Scanning Tunneling Microscope Junction

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Inelastically tunneled electrons from the tip of a scanning tunneling microscope were used to induce S-S bond dissociation of a $(CH_3S)_2$ and lateral hopping of a CH_3S on Cu(111) at 4.7 K. Both experimental results and theoretical calculations confirm that the excitation mechanism of the vibrationally induced chemistry reflects the projected density of states of molecular orbitals that appear near the Fermi level as a result of the rehybridization of the orbitals between the adsorbed molecules and the substrate metal atoms.

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Mode-selective chemistry, whereby a specific chemical bond of a molecule is excited to select a desired reaction pathway, has been widely investigated in the gas phase [1,2]. The scanning tunneling microscope (STM) provides a way to achieve mode-selective chemistry of single molecules adsorbed on surfaces because inelastically tunneled electrons from the STM tip can excite molecular vibrations that lead to a variety of dynamic motions and chemical reactions [3–16]. Molecular vibrations excited through inelastic electron tunneling processes can be accompanied by changes in the differential conductance of a molecule. Inelastic electron tunneling spectroscopy with STM (STM-IETS) [17], which records the second derivative of the tunneling current (I) with respect to bias voltage (V), has proven useful for detecting vibrational signals of individual molecules. However, it does not always reveal all the vibrational modes in the spectra, nor is it applicable to mobile or reactive molecules [4–6,11,15,17]. As an alternative to the STM-IETS, action spectroscopy, which measure the response of vibrationally mediated molecular motion to applied bias voltage, has been used for obtaining vibrational spectra of mobile molecules. Sainoo *et al.* have shown that action spectroscopy can even detect vibrational modes that are not visible using STM-IETS [11].

Persson and Baratoff [18] developed a theory of STM-IETS using an adsorbate-induced resonance model, and before the first experiment by Stipe *et al.* [3], they predicted that the STM-IET spectrum would exhibit a peak-shaped signal at the particular bias voltage where the vibrational excitation of a molecule takes place. Similarly, for the action spectrum obtained from the reaction induced by vibrational excitation, Ueba and Persson [19] have shown that the second derivative of the reaction rate with respect to the bias voltage provides direct access to the vibrational density of states. Moreover, the width of this action spectrum displays the intrinsic vibrational broadening of a single adsorbed molecule on the surface.

Although action spectra offer rich information of this kind, the precise mechanism by which a particular vibrational mode induces molecular reactions by inelastic tunneling electrons has not yet been experimentally examined. Many theoretical attempts to explain the tunneling electron-vibration coupling [20] in a molecule have been based on a resonance model, in which an incident electron becomes temporarily captured by molecular orbitals (MO) localized in a resonant state resulting in excitation of molecular vibrations. Thus, a detailed knowledge of the MOs of the adsorbate is necessary for understanding the underlying mechanism of electron-vibration coupling and for predicting which vibrational mode is actually excited by tunneling electrons.

This Letter reports on quantitative investigations of the vibrationally induced bond dissociation of an isolated $(CH_3S)_2$ molecule and the lateral hopping of an isolated CH_3S molecule adsorbed on the Cu(111) surface with a low-temperature STM. Based on the experimental findings and on density functional theory (DFT) calculations, we discuss how the spatial distribution of MOs of an adsorbate at resonant states can affect electron-vibration coupling and thereby affect the resulting molecular motions and reactions.

All STM measurements were carried out at 4.7 K [21,22] with a low-temperature STM (LT-STM, Omicron GmbH) in an ultrahigh-vacuum chamber ($< 3 \times 10^{-11}$ Torr). Typical conditions for obtaining STM images were $V_{\text{sample}} = -20$ mV and $I_{\text{tunnel}} = 0.2$ nA. The clean Cu(111) surface was exposed to $(CH_3S)_2$ vapor at a temperature below 50 K. After the STM image was taken, the STM tip was positioned over the center of a target molecule. The feedback loop was then turned off, and the tunneling electrons with the defined tunneling current were injected into the molecule. During electron injection, this tunneling current stays constant except when the target molecule reacts, for example, by bond dissociation or molecular hopping, in which case the tunneling current suddenly decreases. In the present study, we calculated the mean time required for bond dissociation (before molecular hopping actually occurred) for each applied bias voltage over 10 trial events with the STM tip in the same position. Multiplying the value of the current (I) and the mean time taken for the reaction (T) gives the number of electrons necessary for the dissociation and for the hopping, from which the reaction yield (R) is determined. The reaction probability was plotted against applied bias voltage to produce an action spectrum. DFT calculations were carried out using the program package DMOL^3 in the Materials Studio of Accelrys Inc. [23,24] for optimizing the adsorption system, and the program code STATE (Simulation Tool for Atom TEchnology) [25–27] for the projected density of states (PDOS) analysis and the drawing of MOs for an isolated $(CH_3S)_2$ and CH_3S on Cu(111).

Individual $(CH_3S)_2$ molecules on the Cu(111) surface appear as elliptic protrusions in STM images, as shown in Fig. 1(a). The intersection points of the mesh in Fig. 1(a) indicate the center positions of the Cu atoms on the surface [21]. By injecting tunneling electrons into the target molecule, we find that a single $(CH_3S)_2$ molecule is broken into two identical ball-shaped protrusions, implying S-S bond dissociation to form two CH_3S molecules [Fig. 1(b)]. For the adsorption site of CH_3S, fcc and hcp hollow sites are equally eligible [28].

Action spectra for dissociation of $(CH_3S)_2$ and $(CD_3S)_2$ are shown in Fig. 1(c). Each spectrum shows one clear threshold voltage at 357.5 mV for $(CH_3S)_2$ and at 275 mV for $(CD_3S)_2$. The threshold voltage at 357.5 mV corresponds to the reported vibrational excitation energy of a C-H stretching mode (ν(C-H)) of the CH_3 group in the molecule. In high-resolution electron energy loss spectroscopy (HREELS), the vibrational frequencies of the ν(C-H) mode are observed at 365 meV for monolayers of $(CH_3S)_2$ on Au(111) and at 366 meV for those on Cu(100) [29,30]. Moreover, the shift of the threshold voltage from 357.5 to 275 mV reasonably corresponds to the isotope shift of ν(C-H) to ν(C-D). Note that the small increase in the reaction yield (-◆- and -◇-) clearly appears at around 410 mV for $(CH_3S)_2$ and at 330 mV for $(CD_3S)_2$, respectively [31]. In the negative bias voltage region, however, the reaction yield was 1.6×10^{-12} and 0.9×10^{-12} for $V_{\mathrm{sample}} = -800$ mV and -600 mV, respectively. This negligibly small dissociation yield in the negative bias voltage region suggests that the reaction yield is strongly influenced by whether the electron was injected to the molecule or extracted from it.

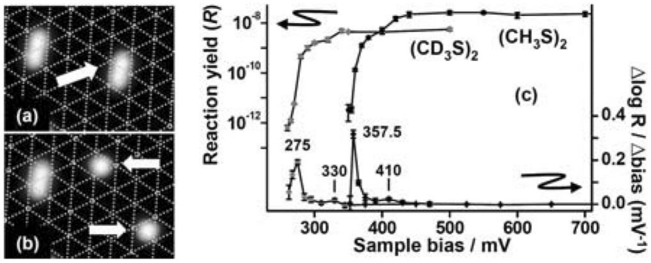

FIG. 1. Topographic STM images of $(CH_3S)_2$ molecules on Cu (111) before (a) and after (b) injection of tunneling electrons. (c) Action spectra for the S-S bond dissociation of $(CH_3S)_2$ and $(CD_3S)_2$ molecules. Initial current was set to 4 nA. The lower traces with "-◆-" and "-◇-" represent the slopes of the reaction for $(CH_3S)_2$ and $(CD_3S)_2$ molecules, respectively. In both spectra, each data point consists of 10 trial events, and thus to obtain these spectra, a total of 130 molecules for $(CH_3S)_2$ and of 110 molecules for $(CD_3S)_2$ respectively were dissociated by tunneling electrons, with the STM tip condition kept constant.

Excited molecular vibrations can cause dynamic processes by overcoming the potential barrier along the reaction coordinate (RC) of a specific adsorbate motion. It has been shown that the vibrational mode along the RC can be excited not only directly but also indirectly through coupling to the higher frequency (HF) vibrational mode excited by tunneling electrons [9]. In the present study, the thresholds observed in the action spectra as a sharp peak at 357.5 meV due to ν(C-H) and as a shoulder at 410 meV due to ν(C-H) + ν(S-S) reveal that S-S bond dissociation in a $(CH_3S)_2$ molecule is induced by excitation of two HF modes, not by direct excitation of the ν(S-S) mode, which is the RC mode for S-S bond dissociation. This is the first observation of an *indirect pathway* for intramolecular bond dissociation on a surface attained by means of tunneling electrons. So far, only a *direct pathway*, resulting from the direct excitation of a specific RC mode, has been reported, in experiments involving O-O bond dissociation of O_2 on Pt(111) [12] and C-H bond dissociation of *trans*-2-butene on Pd(110) [15].

Figure 2(a) shows an STM image of two CH_3S molecules obtained by breaking the S-S bond of a $(CH_3S)_2$ molecule on Cu(111). In previous work, we reported that the injection of tunneling electrons can induce individual CH_3S molecules to hop randomly between the fcc and hcp hollow sites of Cu(111) [22], as shown in Figs. 2(b)–2(d). An action spectrum for the hopping of CH_3S is shown in Fig. 2(e). In the spectrum, threshold voltages are observed at both ±85 mV, the absolute value of which corresponds to the vibrational excitation energy of the C-S stretching mode (ν(C-S)). It is important to note that the reaction yield was identical for both bias polarities, which is very different from what occurs in $(CH_3S)_2$ dissociation. According to DFT calculations, the vibrational excitation energy of ν(C-S) is 85 meV for CS_3S on a Au substrate and 81 meV for CS_3S on a Cu substrate [26,30]. Experimentally, the ν(C-S) mode of various alkylthiolates has been observed at similar energies in HREELS: for example, 88 meV for methylthiolate on Au(111) and 81 meV for butylthiolate and hexylthioate on Au(111) [32]. Since the frustrated translation and/or rotation modes are the RC mode for the motion [7,9], as for the dissocia-

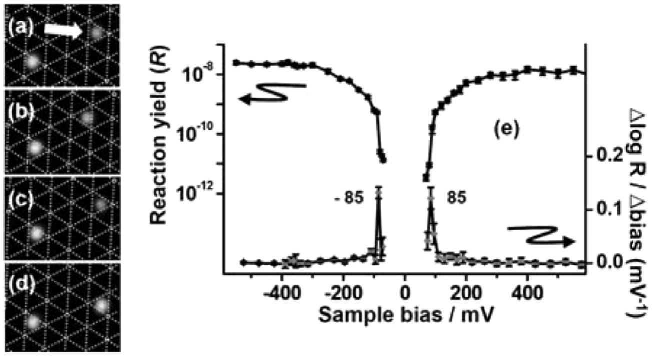

FIG. 2. (a)–(d) Sequential STM images of the hopping of a CH_3S molecule on Cu (111). (e) Action spectrum for the hopping of CH_3S molecules in both positive and negative bias. Initial current was set to 4 nA. The lower trace with "-◆-" represents the slope of the hopping for CH_3S molecules in both positive and negative bias. In the spectrum, each data point consists of 10 trial events; thus, to obtain the spectrum in the positive bias region, a total of 200 CH_3S molecules were counted, with the STM tip maintained in a constant state. A similar number of trials was undertaken for the negative bias region.

tion of the S-S bond in a $(CH_3S)_2$ molecule, the hopping of CH_3S is evidently also the result of an indirect mechanism of RC mode excitation via anharmonic coupling between HF ν(C-S) and RC modes.

As mentioned above, the S-S bond dissociation of $(CH_3S)_2$ is induced by vibrational excitation of the ν(C-H) mode, whereas lateral hopping of CH_3S is not, although both molecules involve C-H bonds of the methyl (CH_3) group. Sainoo *et al.* have pointed out that vibrational modes observed in action spectra can be explained by means of a resonant model of electron-vibration coupling [11]. When a molecule is chemisorbed onto the metal surface, it is distorted by molecule-metal bond formation, and the rehybridized MO consists of several fundamental MOs that appear around the Fermi level (E_f). Thus, to address the applicability of this resonant model to our system, we calculated the projected density of states (PDOS) and the spatial distribution of the MOs for each molecular adsorbate, as shown in Figs. 3(a)–3(d). Figure 3(a) shows that the lowest unoccupied molecular orbital (LUMO) of $(CH_3S)_2$ is located just above E_f, and it also contributes to states near E_f. In addition, the small contributions from the LUMO + 1 and LUMO + 2 states are broadly distributed over the energy region shown. The reaction yield for dissociation showed distinctly different dependence on polarity, where the contribution of the LUMO state apparently dominates, obscuring the relatively small contributions from LUMO + 1 and LUMO + 2 as well as from the HOMO state which is distributed along Cu-S bond. In the case of CH_3S, the HOMO is located just below E_f and, in addition to the LUMO and LUMO + 1, it also contributes to states near E_f, as shown in Fig. 3(c). The reaction yield for hopping is identical for the applied bias voltages of both polarities, which parallels the homogeneous distribution of the DOS across the E_f of the LUMO and/or LUMO + 1, while that of the HOMO contributes much more in the occupied state. The spatial distribution of individual MOs for $(CH_3S)_2$ and CH_3S is depicted in Fig. 3(b) and 3(d), respectively. As shown in Fig. 3(b), the LUMO of $(CH_3S)_2$ is clearly localized at both the S-S and C-H bonds in the molecule, suggesting that a resonantly captured electron in the LUMO will influence the S-S and C-H bond. However, in the case of CH_3S [Fig. 3(d)], there is no contribution of the MOs to the C-H bond in the molecule. This explains why $(CH_3S)_2$ shows a ν(C-H) signal in the action spectrum, whereas CH_3S does not. Figure 3(d) also reveals that the LUMO and LUMO + 1 are rather localized at the C-S bond in CH_3S, which supports the experimental observation of a ν(C-S) signal in the action spectrum of the molecule. It is important to note that the LUMO + 1 and LUMO + 2 of $(CH_3S)_2$ are likewise localized at the C-S bond in the molecule, as shown in Fig. 3(b). One would therefore expect that the ν(C-S) mode also would be detected in the action spectrum of $(CH_3S)_2$. However, in the present study, this was not the case. Especially in the positive bias region, the cross-section with the LUMO state dominates, and as a result, the con-

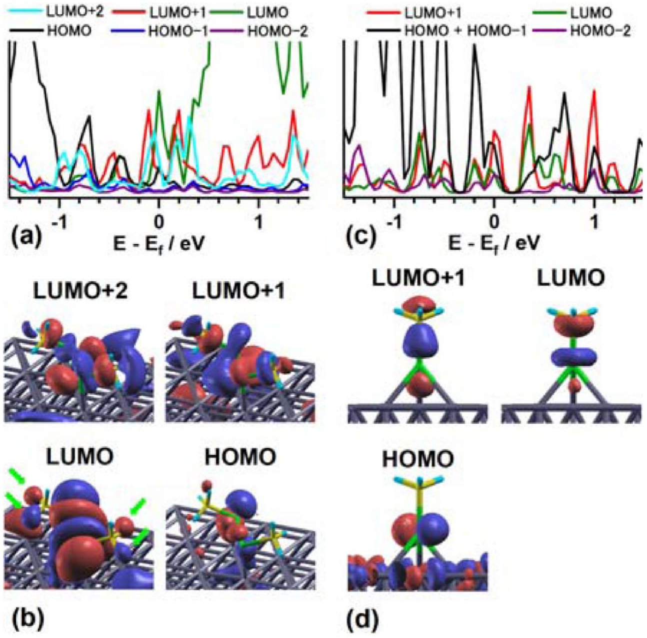

FIG. 3 (color online). (a) PDOS of an isolated $(CH_3S)_2$ molecule on Cu(111). (b) The spatial distributions of LUMO + 2, LUMO + 1, LUMO, and HOMO for an isolated $(CH_3S)_2$ molecule on Cu(111). MOs on C-H bond in $(CH_3S)_2$ molecule are indicated by arrows. (c) PDOS of an isolated CH_3S molecule on Cu(111). (d) The spatial distributions of LUMO + 1, LUMO, and HOMO for an isolated CH_3S molecule on Cu(111). H, C, S, and Cu atoms are drawn in blue, yellow, green, and gray, respectively.

tribution of LUMO + 1 and LUMO + 2 diminishes proportionally. Thus, detailed interpretation of the spatial distribution of individual MOs can successfully explain our experimental action spectra, where the ν(C-H) mode is active for S-S bond dissociation of $(CH_3S)_2$ and the ν(C-S) mode is active for lateral hopping of CH_3S by injecting inelastically tunneled electrons from the tip of an STM.

In conclusion, a combination of quantitative STM experiments and theoretical calculations has been used to investigate the S-S bond dissociation of an isolated $(CH_3S)_2$ molecule and the lateral hopping of an isolated CH_3S molecule on Cu(111) in terms of excitation of molecular vibrations induced by inelastically tunneled electrons. Our experiments reveal that vibrational modes are resonantly excited through a temporal occupation of the MOs by the tunneling electrons and that the molecular vibrations are selectively excited depending on the spatial distribution and the population of the MOs near E_f by hybridization with the substrate metal.

Our present finding that molecular vibrations can be selectively excited depending on the spatial distribution of the MOs near E_f offers a way to systematically realize mode-selective chemistry of individual molecules adsorbed on surfaces, and it also may be applied to characterize molecules bridging two electrodes [33–35].

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