Lateral Hopping of CO on Ag(110) by Multiple Overtone Excitation

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A novel type of action spectrum representing multiple overtone excitations of the $v(M\text{-C})$ mode was observed for lateral hopping of a CO molecule on Ag(110) induced by inelastically tunneled electrons from the tip of a scanning tunneling microscope. The yield of CO hopping shows sharp increases at 261 ± 4 mV, corresponding to the C-O internal stretching mode, and at 61 ± 2, 90 ± 2, and 148 ± 7 mV, even in the absence of corresponding fundamental vibrational modes. The mechanism of lateral CO hopping on Ag (110) was explained by the multistep excitation of overtone modes of $v(M\text{-C})$ based on the numerical fitting of the action spectra, the nonlinear dependence of the hopping rate on the tunneling current, and the hopping barrier obtained from thermal diffusion experiments.

The vibrational excitation of adsorbate on metal surfaces is one of the fundamental processes in various surface dynamic phenomena [1–3]. Action spectroscopy with a scanning tunneling microscope (STM-AS) [4,5] has been widely used to investigate vibration-mediated molecular dynamic behavior on solid surfaces, such as hopping, rotation, desorption, and chemical reaction, at the single-molecule level. In the STM-AS, the vibrational modes leading to molecular motions and reactions can be detected as the dynamic responses to the excitation energy of inelastically tunneled electrons from the STM tip. Ueba [6] and Motobayashi et al. [7] demonstrated that the spectral shape of STM-AS can be expressed by four independent fitting parameters: vibrational energy, reaction order, vibrational broadening factor, and reaction rate. Such underlying physical properties obtained from the spectra allow us further characterization of the microscopic mechanism of single-molecule dynamics. Therefore, the classification of the experimentally observed action spectra using spectral fitting provides an effective way to systematically understand the microscopic mechanisms of vibration-mediated molecular dynamic behaviors on solid surfaces.

To date, the reported action spectra can be classified into four types according to their spectral shapes: single-mode excitation [8–14], multiple-mode excitation [4,15–21], combination-mode excitation [19,21,22], and single-overtone-mode excitation [12], as shown in Figs. 1(a)–1(d), respectively. CO hopping on Pd(110) [9] is classified as a single-mode excitation, because lateral hopping of CO is induced only by excitation of the C-O stretching mode $v(\text{C-O})$. The orientation change of cis-2-butene on Pd(110) [4,7] is a multiple-mode excitation, where the excitations of the following four

vibrational modes can independently contribute to the change of adsorption configuration among equivalent molecular orientations: metal-carbon stretching $v(M\text{-C})$ and C-C stretching $v(\text{C-C})$, modes for low-barrier motion, and bending modes in CH_3, $\delta(CH_3)$, and $v(\text{C-H})$ for high-barrier motion. S-S bond dissociation in dimethyl disulfide $(CH_3S)_2$ on Cu(111) [21] provides a combination-mode excitation action spectrum, in which the threshold bias voltage corresponding to the excitation of the combined $v(\text{C-H})$ and S-S stretching $v(\text{S-S})$ modes was observed in addition to $v(\text{C-H})$ excitation. The single-overtone-mode excitation STM-AS has been reported for the desorption of NH_3 on Cu(100) [12], in which the excitation of the first overtone of the $N\text{-}H_3$ umbrella mode overcame the desorption barrier, and was clarified as a single-electron process.
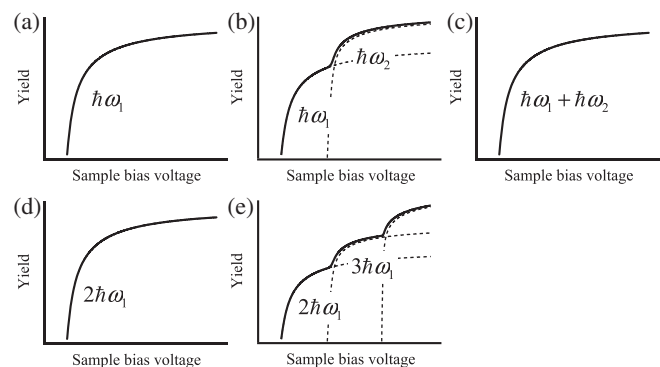

FIG. 1. Schematic illustrations of five types of action spectra: (a) Single-mode excitation; (b) multiple-mode excitation; (c) combination-mode excitation; (d) single-overtone-mode excitation; and (e) multiple-overtone-mode excitation.

We herein report a novel action spectrum, multiple-overtone-mode excitation [Fig. 1(e)], for the lateral hopping of a CO molecule on Ag(110). STM-AS and spectral fitting results clearly indicate that excitation of multiple overtone modes of $v(M\text{-}C)$ composed not only of a first overtone mode but also of higher overtone modes, i.e., second and fourth overtone modes, contributes to inducing lateral hopping motion. The estimated energy barrier for hopping motion from STM-AS agrees well with that obtained by thermal hopping experiments. Our findings of molecular motions induced by exciting a series of overtone modes unveil a novel vibrational excitation pathway leading to molecular dynamic process on a metal surface.

Experiments were performed using a low-temperature STM (LT-STM, Omicron GmbH) equipped with an ultra-high vacuum (UHV) chamber at 5 K and 3×10^{-11} Torr. The lateral hopping motion of an isolated CO molecule was induced by injecting tunneling electrons from an electro-chemically etched tungsten tip to the center of a molecule in the STM image with an open feedback loop. The clean surface of Ag(110) single crystal was prepared using cycles of Ar^+ ion sputtering and annealing at 750 K. CO molecules were exposed to the Ag(110) surface through a variable leak valve located inside the STM chamber.

Prior to the STM-AS measurements, the adsorption properties, such as the adsorption site, vibration modes, and thermal diffusion barrier of a CO molecule on a Ag(110) surface were examined (see Sec. I in the Supplemental Material [23] for details, which includes Refs. [24,25]). The CO molecules were adsorbed on the on-top site of the Ag lattice, and imaged as a round depression as shown in Fig. 2(a) [see also Figs. S1(a) and S1(b) [23]]. The vibrational energies of two hindered modes, i.e., hindered translation [HT, 7.5 meV] and hindered rotation [HR, 18.5 meV], and two stretching modes, i.e., metal-C stretching [$v(M\text{-}C)$, 31 meV] and internal stretching [$v(C\text{-}O)$, 261 meV] were measured and assigned by means of inelastic electron tunneling spectroscopy with STM (STM-IETS) and high-resolution electron energy loss spectroscopy (HREELS), respectively (see Fig. S1). The activation energy for CO diffusion was also estimated to be 133 ± 8 meV with thermal diffusion experiments using STM, in which the CO diffusion rate was measured in the temperature range from 42.0 to 44.5 K. (see Sec. II in the Supplemental Material [23] for details, which includes Refs. [26,27]).

STM-AS measurements were carried out for the vibration-induced hopping of CO molecules on Ag(110). Figure 2(a) shows that a target CO molecule (marked "**A**") hopped to a neighboring on-top site along the $[1\bar{1}0]$ direction by injecting tunneling electrons with a tunneling current I of 1 nA and a sample bias voltage V of 250 mV. A current trace was monitored during the lateral hopping motion to observe the sudden change during the hopping event, as shown in Fig. 2(b). The hopping yield $Y(V)$ and
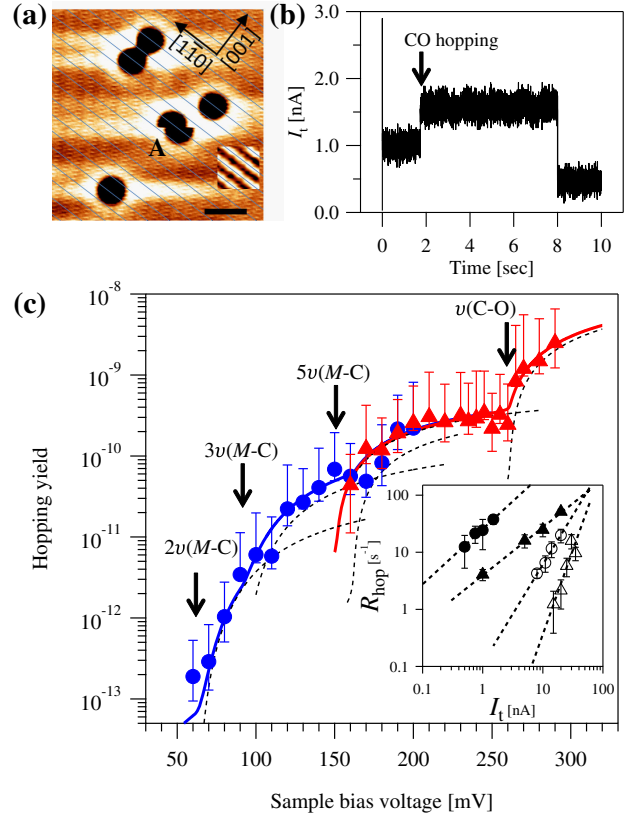

FIG. 2. (a) Topographic STM image of five CO molecules on an Ag(110) surface (5×5 nm^2, scale bar = 1 nm, $V_s = 100$ mV, $I_t = 1$ nA). Inset-image obtained from a CO-terminated tip shows atomic rows along the $[1\bar{1}0]$ direction of Ag(110), represented by blue solid lines. The CO molecule hopped along the $[1\bar{1}0]$ direction by injecting tunneling electrons, as marked by "**A**." (b) Tunneling current monitored during the injection of tunneling electrons ($V_s = 250$ mV, $I_t = 1$ nA) over the center of the "**A**" CO molecule with open feedback loop. (c) Action spectra for lateral hopping of a CO molecule as a function of sample bias voltage under constant tunneling currents (I_t) of 1 (filled triangle) and 20 nA (filled circle). Solid lines indicate the spectral fitting results of the experimental data. The inset shows the hopping rate (R_{hop}) of a CO molecule as a function of tunneling current (I_t) for sample bias voltages 90 (open triangle), 140 (open circle), 180 (filled triangle), and 280 mV (filled circle). The dashed lines in the inset represent least squares fits to the data, and correspond to the powers (n) in nonlinear power-law dependence, $R \propto I^n$.

rate $R(I)$ were estimated from the current traces as functions of V and I, respectively. The $Y(V)$ provides sample bias voltages corresponding to the active vibrational modes responsible for the molecular hopping motion [4,7]. In addition, $R(I)$ exhibits a power-law dependence on I and on the reaction order n, $R(I) \propto I^n$ [11,12,28], and therefore describes the number of electrons required for an event. Figure 2(c) shows the action spectra obtained at a tunneling current of 20 nA (blue circles). With a sample bias voltage greater than ~200 mV, the lower tunneling current of 1 nA

(red triangles) was applied due to significantly faster hopping motions under the measurement conditions. The action spectra exhibited a novel feature for the vibration-induced hopping of CO molecules on Ag(110), with a significant increase in $Y(V)$ at sample voltages of ~70, 100, 150, and 260 mV (black arrows). The current dependence of $R(I)$ was presented in the inset of Fig. 2(c). The estimated reaction orders n were 2.96 ± 0.09, 1.73 ± 0.08, 0.84 ± 0.04, and 0.97 ± 0.2 for sample bias voltages 90, 140, 180, and 280 mV, respectively. That is, the lateral hopping motions for each energy region, i.e., (i) 70 mV $< V_s <$ 100 mV, (ii) 100 mV $< V_s <$ 150 mV, (iii) 150 mV $< V_s <$ 260 mV, and (iv) $V_s >$ 260 mV, are induced as three-, two-, one-, and one-electron processes (n = 3, 2, 1, and 1), respectively (see Sec. III in the Supplemental Material [23] for the details of noninteger number n as a reaction order, which includes Refs. [29–35]).

Spectral fitting of the STM-AS spectra was then performed to extract additional information regarding the hopping mechanism. The $Y(V)$ including the multielectron excitation process can be defined as [6,7]

$$Y(V) = K_{\text{eff}} \frac{F(V, \hbar\Omega, \sigma_{\text{ph}})^n}{V}, \qquad (1)$$

where K_{eff}, $\hbar\Omega$, σ_{ph}, and n indicate the effective prefactor, the vibrational energy responsible for the excitation, the vibrational broadening factor, and the reaction order, respectively. In this formula, $F(V, \hbar\Omega, \sigma_{\text{ph}})$ can be derived by integrating twice the effective vibrational density of states (DOS) expressed with the Lorentzian function (see Sec. IV in the Supplemental Material [23] for details, which includes Ref. [36]). The estimated vibrational energies are 61 ± 2, 90 ± 2, 148 ± 7, and 261 ± 4 meV, as indicated by the solid and dashed lines in Fig. 2(c). The STM-AS results were well reproduced with a set of parameters (K_{eff}, $\hbar\Omega$, σ_{ph}) only while using the reaction orders n obtained from the current dependence of $R(I)$. For example, where $I_t = 1$ nA, the fitting result with a set of parameters (7.9×10^{-10}, 148 meV, 1 meV) for 150 mV $< V_s <$ 260 mV and (2×10^{-8}, 261 meV, 1 meV) for 260 mV $< V_s$ gives the best-fitting spectra for the experimental results. The estimated threshold energies do not correspond to any fundamental vibrational modes except 261 ± 4 meV [v(C-O), see HREELS data in Fig. S1(d)]. However, as the first three threshold energies are very close to the multiple values of the $v(M$-C) mode, meaning that the $v(M$-C) overtone modes can be considered corresponding vibrational modes.

We herein focused on anharmonicity to describe the dynamic behavior of the observed CO hopping motions on Ag(110). The harmonic oscillator model is sufficient to examine the vibrational excitations from ground state to first ($v = 1$) or second ($v = 2$) excited state [11,37]. However, when the vibrational quantum number of the excited state reaches the fourth overtone ($v = 5$), the influence of anharmonicity on the potential energy surface for the
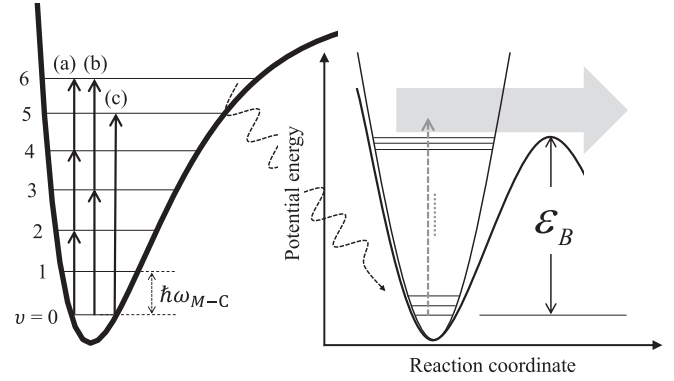

FIG. 3.   Schematic representation of vibrational excitations of multiple overtone modes originating from the metal-molecule stretching mode, $v(M$-C): (a) First, (b) second, and (c) fourth overtone modes. Lateral hopping of a CO molecule is induced by an intermode coupling between overtone modes of $v(M$-C) and the reaction-coordinate (RC) mode, i.e., the hindered-translation (HT) mode.

hopping motion and the individual vibrational energy levels involved in the overall excitation process cannot be ignored. The Morse potential energy function can be used to describe the energy levels in the presence of anharmonicity as shown in Eq. (2):

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) - \hbar\omega_e\chi_e\left(v + \frac{1}{2}\right)^2, \qquad (2)$$

where v, $\hbar\omega_e$, and χ_e are the vibrational quantum number, equilibrium vibrational energy, and anharmonicity constant, respectively [38]. Applying the obtained threshold energies into Eq. (2), the $\hbar\omega_e$ and χ_e for $v(M$-C) were calculated as 32 ± 0.5 meV and 0.0156 ± 0.0051. The estimated $\hbar\omega_e$ value agrees with HREELS data, i.e., 31 meV, measured at 0.5 ML of coverage [see Fig. S1(d)]. There has, however, been no previous report on the χ_e value for the $v(M$-C) of CO adsorbed on the metal surface. We therefore compared the χ_e for the $v(M$-C) estimated from our action spectra with the reported χ_e values for the v(C-O) of Ru(001) [39] and Ir(111) [40] (0.0067 and 0.0065, respectively). These values are smaller than that of our result, due to the weaker bond strength leading to a larger anharmonicity [38,39].

Based on the our results, the hopping mechanism corresponding to the first three threshold energies can be described schematically as shown in Fig. 3. The detailed mechanism through multistep excitations of $v(M$-C) overtone modes can be expressed as follows: (a) Triple-step excitation of the first overtone, $2v(M$-C), for 61 ± 2 mV $< V_s <$ 90 ± 2 mV; (b) double-step excitation of the second overtone, $3v(M$-C), for 90 ± 2 mV $< V_s <$ 148 ± 7 mV; and (c) single-step excitation of the fourth overtone, $5v(M$-C), for 148 ± 7 mV $< V_s <$ 261 ± 4 mV. At the highest energy region, $V_s >$ 260 mV, CO hopping is induced by a single-step excitation of v(C-O). The energy of a vibrationally excited

CO molecule then transfers to the reaction-coordinate (RC) mode (i.e., the HT mode) through intermode coupling, and finally CO overcomes the energy barrier for the lateral hopping motion, as reported for CO hopping on Pd(110) [9]. It is worth noting that there has been no report on the molecular motions by excitation of an entrance vibrational mode that has a lower energy than the reaction barrier (see Sec. V in the Supplemental Material [23] for details, which includes Ref. [41]). From this model, the energy barrier (ε_B) for CO hopping on Ag(110) was estimated as 122 meV $< \varepsilon_B <$ 148 meV. The maximum value should be smaller than the vibrational energy of $5v(M\text{-C})$, while the minimum value should be larger than twice the vibrational energy of $2v(M\text{-C})$. This result is in good agreement with the energy barrier (133 ± 8 meV) obtained from the thermal diffusion experiments (see Fig. S2). The absence of a threshold energy corresponding to the third overtone mode, $4v(M\text{-C})$, in the action spectra can also be understood using the energy barrier ε_B. From the estimated values of $\hbar\omega_e$ and χ_e, the energy level of the third overtone, $4v(M\text{-C})$, is expected to lie between 118 and 120 meV. Thus, a single excitation of $4v(M\text{-C})$ is not sufficient to overcome the energy barrier, and so a double-step excitation process is required for the lateral hopping. However, this may be energetically unfavorable compared to the corresponding excitation process of $3v(M\text{-C})$.

Finally, we investigated the participation of multiple overtones of the $v(M\text{-C})$ mode in inducing lateral hopping of a CO molecule. Whereas CO vibrational modes on various metal surfaces have been investigated using both STM-IETS [42–46] and STM-AS [9], the detection of the $v(M\text{-C})$ mode has not yet been achieved. In particular, CO hopping on Pd(110) was induced only by excitation of the $v(C\text{-O})$ mode [9]. Herein, we have demonstrated that a series of $v(M\text{-C})$ mode overtones are detectable by STM-AS for CO hopping on Ag(110). Our observation implies either that the lifetime of $v(M\text{-C})$ overtones is sufficiently long to be multiply excited, or that the intermode coupling constant with the RC mode allows energy transfer to the RC mode, triggering molecular hopping. Although quantitative information on both the lifetime and intermode coupling constants of vibrationally excited states of CO molecules adsorbed on solid surfaces has been experimentally obtained using infrared absorption spectroscopy (IRAS) measurements [47,48], it remains a challenge to overcome low infrared cross sections of the $v(M\text{-C})$ mode and intrinsically poor spectral sensitivity at low-frequency ranges [49]. Alternatively, the intermode coupling between fundamental vibrational modes of a molecule on a solid surface can be investigated by theoretical computations, as demonstrated by Lorente *et al.* [50]. In particular, the computation was performed to explain the difference between the hopping behavior of CO on Cu(110) and on Ag(110), in which CO hopping by vibrational excitation is only feasible on the Ag(110) surface [51]. The computational results, however, indicated that both the $v(C\text{-O})$ lifetime and its intermode coupling with the RC mode cannot resolve significantly higher CO hopping capabilities on Ag(110) compared to the immobility on Cu(110). This is the case even though $v(C\text{-O})$ has been considered the most important excitation channel for inducing the hopping motion, as reported for the CO/Pd(110) system [9]. However, our STM-AS results clearly indicate that the lateral hopping motion can be induced by the (multiple) excitation of an entrance vibration mode exhibiting a lower energy than the hopping barrier. Further theoretical investigations into the intermode coupling between overtones of the $v(M\text{-C})$ mode and hindered vibration modes are required to study the above-mentioned long-standing issue regarding CO hopping on coinage metal surfaces.

In conclusion, we investigated the lateral hopping mechanism of individual CO molecules adsorbed on a Ag(110) surface using action spectroscopy with low-temperature STM. We found that the lateral hopping of a CO molecule can be induced not only by the excitation of the $v(C\text{-O})$ mode but also by vibrational excitations of several overtone modes of $v(M\text{-C})$, and in particular the higher overtone modes. To the best of our knowledge, our result is the first observation of molecular motion induced by vibrational excitations of multiple overtone modes. Our results not only open new opportunities to utilize higher adsorbate overtone modes for triggering elementary surface chemistry processes but also stimulate further spectroscopic and theoretical investigation into gaining a deeper insight into underlying surface dynamics, such as energy transfer mechanisms and the influence of the substrate, thus leading to efficient excitations of multiple overtone modes.

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