Abstract I describe a brief summary of quantum mechanics and principles of scanning tunneling microscopy (STM) in this chapter. Quantum tunneling is an important concept to describe the transportation of small particles, like electron and hydrogen. In Sect. 2.1 I focus on H-atom tunneling in a double minimum potential that is the simplest but a ubiquitous system in physics and chemistry. Quantum tunneling of electron directly relates to the principle of the STM. In Sect. 2.2 the principles and applications of STM are described. I focus on the inelastic electron tunneling process in an STM junction, which can be applied to the vibration spectroscopy and reaction control of single molecules.

Keywords Quantum tunneling · Double minimum potential · Scanning tunneling microscope/spectroscopy · Inelastic electron tunneling

2.1 Quantum Mechanics

2.1.1 Basics of Quantum Tunneling

Quantum tunneling is derived from the concept of quantum mechanics, where a particle can pass through a barrier that is classically insurmountable. This is a result of the wave-particle duality of matter. Quantum tunneling becomes pronounced in light particles such as electron and H atom.

Figure 2.1 shows the simplest model in which a particle tunnels through a one-dimensional rectangular barrier. The time-independent Schrödinger equation of the particle is written by

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x) \] (2.1)
\[
\frac{d^2}{dx^2} \psi(x) = \frac{\hbar^2}{2m} (V(x) - E) \psi(x)
\]  
(2.2)

where \( m \) is the mass, \( \psi(x) \) is the wave function, \( E \) is the energy of the particle and \( V(x) \) is the potential. In the region of \( V(x) < E \)

\[
\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}
\]  
(2.3)

\[
\kappa^2 = -\frac{2m(V(x) - E)}{\hbar^2}
\]  
(2.4)

The wave function shows the oscillation characterized by the wave vector \( \kappa \). On the other hand, in the region of \( V(x) > E \)

\[
\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}
\]  
(2.5)

\[
\kappa^2 = \frac{2m(V(x) - E)}{\hbar^2}
\]  
(2.6)

The wave function no longer shows the oscillation, and it monotonically decreases with the decay constant \( \kappa \). For light particles we have a chance to find the particle beyond the classically impenetrable barrier, and the wave function starts oscillating again. The transmission probability \( T \) of a particle can be analytically-derived in this simple model, which is given

\[
T = \left\{1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\epsilon(1 - \epsilon)} \right\}^{-1}
\]  
(2.7)

where \( \epsilon = E/V \), and \( L = (x_2 - x_1) \) is the barrier width of a one-dimensional rectangular potential. If we assume \( \kappa L \gg 1 \), corresponding to a barrier of sufficient height and width,

\[
T \approx 16\epsilon(1 - \epsilon)e^{-2\kappa L}
\]  
(2.8)
The transmission probability decreases exponentially with an increase of the mass, $m^{1/2}$, and the barrier width, $L$. Thus a significant isotope effect between H and D (deuterium) is expected in the dynamical processes.

The one-dimensional rectangular barrier is an oversimplified model system. The barrier that smoothly varies, as shown in Fig. 2.2, is a more realistic question. Using the WKB approximation, the tunneling probability $D(E)$ of a particle that has the total energy $E$ in a one-dimensional potential barrier $V(x)$ is expressed by

$$D(E) = \exp\left\{-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)}\,dx\right\}$$

(2.9)

where $x_1$ and $x_2$ is the classical turning points, and $(x_1-x_2)$ corresponds to the barrier length. In the WKB approximation the Planck constant is regarded as a small number. Therefore this approximation is called semi-classical and valid when the total energy is significantly lower than the barrier. It is noted that the WKB approximation is restricted to one-dimensional problems, thus it cannot be applied to multi-dimensional problems that are much more likely in chemical and biological processes.

In addition to the mass effect, the zero point energy (ZPE) must be considered when we treat the kinetics of H and D. Assuming a harmonic potential, the ZPE is given by

$$E_0 = \frac{1}{2} \hbar \omega, \quad \omega = \sqrt{\frac{k}{m}}$$

(2.10)

where $\omega$ is the vibrational frequency and $k$ is the spring constant. According to (2.10), the ZPE of D atom is smaller by the factor of $(1/2)^{1/2}$ than that of H. This reduction of the ZPE also lowers the transmission probability of D atom through the increase of the effective barrier.
Symmetry is important to understand diverse concepts and laws of nature. Here I focus on the role of symmetry in H transfer. The symmetry of the potential landscape is a key to the mechanism involving quantum tunneling. The simplest, but a ubiquitous system in physics and chemistry is a symmetric double minimum potential (Fig. 2.3), where we can consider two wave functions |\( W_1 \rangle \) and |\( W_2 \rangle \) with a specific Hamiltonian \( H_i \) (\( i = 1 \) or \( 2 \)) in each potential well where the eigenenergy is given by \( H_i | \Psi \rangle = E_0 | \Psi \rangle \). If each of the two states is independent, the wave packet is localized in each of the potential well for all time. Now we take into account the transfer of a wave packet between two wells and introduce the transition matrix \( \hat{H}_{ij} \); \( i,j=1 \) or \( 2; i \neq j \) that transfers the wave packet into another well. As long as the matrix element \( H_{ij} = < \Psi_i | \hat{H}_{ij} | \Psi_j \rangle = 0 \), each of the two states degenerates into the eigenstate with its eigenenergy of \( E_0 \) (Fig. 2.3a). However, this situation is varied if \( H_{ij} \neq 0 \) (Fig. 2.3b), where |\( W_1 \rangle \) and |\( W_2 \rangle \), are no longer the eigenstate of the system and the eigenfunctions are given by the symmetric (gerade) and anti-symmetric (ungerade) linear combination of |\( W_1 \rangle \) and |\( W_2 \rangle \).

\[
|g\rangle = \frac{1}{\sqrt{2}} (|\Psi_1\rangle + |\Psi_2\rangle), \quad |u\rangle = \frac{1}{\sqrt{2}} (|\Psi_1\rangle - |\Psi_2\rangle)
\]

The corresponding energy levels are split into

\[
E_k = E_0 \pm |H_{12}|
\]

where \( k \) is \( g \) (gerade) or \( u \) (ungerade) and the lower or upper energy levels belongs to the symmetric or anti-symmetric state. \( |H_{12}| \) corresponds to the energy splitting. Given that the system is initially in the state of |\( \Psi_1 \rangle \), the system shows a periodic motion between |\( \Psi_1 \rangle \) and |\( \Psi_2 \rangle \) states because the |\( \Psi_1 \rangle \) is no longer an eigenstate of the system. Then the probabilities finding the wave packet in |\( \Psi_1 \rangle \) and |\( \Psi_2 \rangle \) change according to

\[
P_1 = \cos^2(H_{12}|t|), \quad P_2 = \sin^2(H_{12}|t|)
\]
The frequency of this oscillation \( v_t \), the so-called tunneling frequency, is given by

\[
v_t = \frac{|H_{12}|}{\pi}
\]

This periodic oscillation is called the coherent tunneling.

Hydrogen (proton) tunneling has been derived from the theory of the one-dimensional symmetric double oscillator [1]. The separation between the two states are characterized by \( \Delta E = h v_t \) (\( h \) is Planck’s constant). The transfer time \( \tau \) is related to the tunneling frequency by \( \tau = 1/2v_t \). The tunneling splitting strongly depends on the barrier height and width. The energy level splitting due to coherent tunneling has been observed in many model systems such as small water clusters [2], NH\(_3\) [3], tropolone [4, 5], and malonaldehyde [6–8] in the gas phase, using rotation-vibration spectroscopy. The tunneling splitting, namely the tunneling frequency, varies from \( 10^{12} \) Hz to a few Hz depending on the system.

### 2.1.3 Tunneling in an Asymmetric Double Minimum Potential

Surrounding environments or external perturbations alter the symmetry of the potential landscape of \( \text{H} \) transfer. In condensed matter, intermolecular interactions commonly vary the symmetric potential, resulting in an asymmetric potential as depicted in Fig. 2.4a. In this situation, the wave packet of hydrogen is forced to be localized in one potential well. However, tunneling is still possible at the excited state. This situation is depicted in Fig. 2.4a. A vibrational excitation generates the wave packet in the excited state, which is further transferred to another well via tunneling. This process is no longer coherent.

In liquid, the situation becomes much more complicated. The effective symmetry of the potential is continuously altered by surrounding solvents. This situation is
depicted in Fig. 2.4b. An alternative description about H atom transfer in liquid was proposed by Borgis and Hynes [9, 10]. As shown in Fig. 2.4c the asymmetric single or the double well potential, where the wave packet of hydrogen is localized in one well, is continuously converted into symmetric potential by surrounding solvents. But the strong interaction between the molecules results in a significantly reduced barrier, where the ZPE overcomes the barrier. In this situation H transfer takes place adiabatically and hydrogen motion is no longer governed by tunneling.

2.2 Scanning Tunneling Microscope

2.2.1 Overview

STM is a powerful tool to image conductive surfaces with an atomic resolution. In principle, an optical microscope cannot realize such a high resolution due to its diffraction limit. STM was developed in 1982 by Binnig and Rohrer at IBM Zürich Research Laboratory [11]. They were awarded the Nobel Prize in 1986 for the development of the STM. In STM, the highest resolution is considered to be 0.1 nm laterally and 0.01 nm vertically. STM set a new direction for nanoscience and nanotechnology and has continued to evolve as a fascinating tool to investigate physical, chemical, and biological processes at the spatial limit.

STM is based on the concept of quantum tunneling of electron. When a conducting tip having an atomically sharp apex, is brought very close (few Å) to the conductive surface while a bias voltage is applied between the tip and the surface, electrons can tunnel through the barrier between them. The tunneling current is described as a function of the relative distance between the tip and surface, the applied voltage, and the local density of states (LDOS) of the tip and surface. Since the tunneling current depends exponentially onto the tip-surface distance, the current has a considerably sensitivity to the surface corrugation. If the tip apex consists of a single or few atoms, it has an atomic level sensitivity against the surface corrugation. The STM image is acquired by scanning the surface with controlling the distance between the tip and surface. Figure 2.5 shows a schematic illustration of the basic STM setup. The STM measurement is carried out by following manner; first, bias voltage is applied between a sharp tip and a conductive substrate, and then the tip is brought close to the substrate using a coarse piezo control system of the tip along z direction (surface normal). This coarse motion is turned off when the tip and the surface become sufficiently close (few Å) and the tunneling current is detected. At the tunneling region, the fine control of the tip in all three dimensions is required to maintain the tip-sample distance \( d \) (3 < \( d \) < 10Å). Once the tunneling junction is established, the bias voltage and the tip position with respect to the surface can be varied. The usual bias voltage to image molecules chemisorbed on surfaces is in a range of \( \pm 2 \) V. Two different modes to obtain STM image exist. First, the tip is scanned with constant \( z \) height (constant height mode).
The variation of the tunnel current is recorded as the tip is scanned along the surface. Second, the tip is scanned with the tunneling current kept constant during the scanning (constant current mode). In this case, the $z$ position of the tip is controlled via the feedback loop and it varies during the measurements, and this variation of the $z$ position is recorded to produce an STM image. Thus the STM image corresponds to topography across the surface and gives approximately constant LDOS of the surface; this means the contrast of the image is due to variations in the density of states. The constant height mode, with the voltage and height both kept constant, gives an image of current variation over the surface, which can also be related to the LDOS. The benefit of using a constant height mode is that it can record an image faster as the tip is not required to precisely follow the corrugation of the surface. Thus the constant height mode is usually employed in a high-speed measurement which enables us to record an image at a video rate.

In addition to imaging a conductive surface, since the tunneling current stems from the LDOS, we can extract the local electronic structure of a surface by sweeping the bias voltage and measuring current with fixed the tip at a specific location. This measurement is called scanning tunneling spectroscopy (STS). The technical details and the applications of the STM were already summarized in several good books [12–15]. STM and its derivative techniques, called the scanning probe technique including the atomic force microscopy and the scanning near optical field microscopy, will keep on evolving as a base technology of nanoscience.

### 2.2.2 Tunneling Current

STM relies on the electric current originated from quantum tunneling of electron flowing between a conductive tip and surface. For a proper interpretation of an
STM image it is essential to understand how tunneling current is described in the STM junction. Figure 2.6 illustrates a typical tunnel junction consisted of metal–insulator (vacuum gap)-metal system. Tunneling current can be expressed by

\[ I \propto \int_{0}^{eV} e \rho_{l}(E) \rho_{r}(-eV + E) T(R, eV, E) dE \]  

(2.11)

where \( \rho_{l(r)} \) is the density of state of the left(right) electrodes, corresponding to a conductive substrate and tip in STM, \( E \) is the energy of electrodes with respect to the Fermi level, \( V \) is a bias voltage applied between the tip and surface, and \( T \) is a tunnel probability which can be expressed using the WKB approximation,

\[ T = \exp \left\{ -\frac{2d\sqrt{2m}}{\hbar} \sqrt{\frac{\phi_{l} + \phi_{r}}{2} - E + \frac{eV}{2}} \right\} \]  

(2.12)

where \( d \) is the distance between the electrodes, thus the thickness of the potential barrier, \( \phi_{l(r)} \) is the work function of the electrodes. From Eq. (2.12), tunneling current shows an exponential dependence onto the electrode distance. As a consequence, tunneling current is very sensitive to \( d \).

According to Eq. (2.11) the tunneling current in STM reflects the LDOS of a tip and substrate. If the change in an LDOS of a substrate is induced by the adsorption of molecules, tunneling current is significantly affected in the vicinity of the molecule. With the adsorption of molecule, the charge transfer between the molecule and surface occurs, inducing molecule-induced state near the Fermi level. However, the interpretation of an STM image of molecules on a surface is not straightforward. For instance, carbon monoxide molecule is observed as depression in STM image, meaning the reduction of the density of state near the Fermi level. On the other hand, water molecule is observed as protrusion, meaning
the increase of the DOS near the Fermi level. The explanation has been demonstrated by using theoretical calculations in the past [16]. The appearance of STM image also depends on the tip conditions. For instance, if a molecule adsorbed on the tip apex, the STM image is significantly changed. Therefore we have to discuss an STM image very carefully and a combination of first principle calculations is quite beneficial.

2.2.3 Inelastic Electron Tunneling

In the electron tunneling described above, we considered the situation in which electrons are transferred between the electrodes without energy loss. This process is called elastic process. However, when oscillators, i.e. molecules, exist in the tunneling gap, tunneling electrons can interact with them. If the tunneling electron has enough energy to excite the vibration, it gives a part of energy to the vibrational excitation during the tunneling. In this process the energy of the electron is different between before and after the tunneling, which is called inelastic electron tunneling (IET) process. In the IET process a vibrational excitation opens an additional channel for tunneling electrons (Fig. 2.7a), giving rise to a substantial increase in the total current. The IET process was originally observed in metal-oxide-metal junctions where the molecules are included in the oxide layer [17, 18] as illustrated in Fig. 2.7b. We now turn to a bias voltage dependence of tunneling current in the tunnel junction including an oscillator (molecule) (Fig. 2.7c–e). Below a vibrational threshold \( (eV < \hbar \omega) \), the tunneling current increases almost linearly with ramping of the bias voltage, which is attributed to the elastic component. On the other hand, above the threshold \( (eV = \hbar \omega) \), electrons also tunnel via an inelastic channel. The probability passing the inelastic channel increases with the increase of bias voltage. Accordingly, the total current, including both elastic and inelastic components, shows a kink at \( eV = \hbar \omega \) (Fig. 2.7c). The kink becomes the step and the peak in the conductance \( (dI/dV) \) (Fig. 2.7d) and the differential conductance \( (d^2I/dV^2) \) spectra (Fig. 2.7e), respectively. In general, since the fraction of the inelastic component is very small, like the conductance change is a few % (Fig. 2.7d). The peak in \( d^2I/dV^2 \) spectra indicates the vibrational energy and the intrinsic width, which is called IET spectra. The peak position, that is vibrational energy, corresponds to the signature of molecules and also represents the interaction with a substrate and surrounding conditions. Therefore we can chemically identify the species and speculate the structure of molecules in a tunnel junction. The peak width arises from three different contributions; the intrinsic width \( \Gamma \) of the vibration, the thermal broadening \( k_BT \) and the additional broadening depending on experimental conditions. The intrinsic width of vibration modes for adsorbates is expected to be the order of 1 meV or greater in surface species, with the peak profile described by a Lorentzian function. On the other hand, the thermal broadening is described by the Gaussian profile. Since the measurement of IETS is based on the lock-in detection, we also have to
take the broadening due to the modulation voltage into account. The resolution of IETS is usually governed by the thermal effect and modulation voltage and the total width in the $d^2I/dV^2$ signal is represented by the following Eqs. [19–22]

$$W = \sqrt{(1.7V_{\text{rms}})^2 + (5.4k_B T)^2 + \Gamma^2}$$

(2.13)
where $V_{\text{rms}}$ is the modulation voltage, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The typical resolution of IETS is expected to be 1-4 meV at low temperature ($\sim 5$ K).

### 2.2.4 STM-IETS

The capability detecting molecular vibrations by combining STM and IETS was already mentioned in the 1980s. Since tunneling electrons in STM pass through an area that is smaller than a single molecule, in principle, STM-IETS is able to measure molecular vibrations within a single molecule. The first result was reported in 1998 by Stipe et al. [23] and the C–H(D) stretch mode was clearly observed with the correct ratio of the isotope substitution. This result demonstrated the STM ability to be used as not only a microscope but also a chemically sensitive tool. At the same time, the result provided following questions. (i) Why only the C–H stretch mode is detected? (ii) What determines the shape of spectra? (i) is related to the selection rule, which is important and useful in vibrational spectroscopy for understanding the molecular states. (ii) is related to fundamental processes of a vibrational excitation/de-excitation of adsorbates. To answer these questions several experimental and theoretical attempts have been devoted in the last decade. The basic concept describing the elementary process of STM-IETS dates back to theoretical works reported in the late 1980s [24, 25]. Persson and Demuth first discussed the inelastic tunneling with the scheme of dipole scattering theory using Bardeen’s formula for electric current [24]. After that, Persson and Baratoff showed that the resonant tunneling via adsorbate induced states is a dominant channel for inelastic process and the inelastic fraction of electronic current is associated with the vibrational damping rate due to the electron–hole pair excitation [25].

Figures 2.8a illustrates an STM junction consisted of a tip, substrate, and molecule chemisorbed on the substrate. The molecule forms the molecule-derived state $\rho_a$ around the Fermi level $E_F$ of the substrate, which is derived form a molecular orbital $\lambda_a$ [16]. Such molecular-induced resonances frequently occur in the vicinity of $E_F$ [26]. The width of the molecular state $\Gamma$ is determined by the strength of the interaction between a molecule and an electronic state of an electrode. Tunneling electrons pass through the molecule-derived state $\rho_a$. When an electron has tunnel into $\rho_a$, it is temporary trapped in $\rho_a$ for a time $t \sim \hbar/\Gamma$. If a tunneling electron has enough energy to excite a molecular vibration ($\hbar\omega$), it becomes possible to leave a vibrational excitation in the molecule and the electron inelastically-tunnels, which eventually opens an additional channel for the electron transport and results in the increase of a total current. This resonant tunneling model was experimentally examined by Kawai and her co-workers at RIKEN, Japan. They showed that the vibrational excitation depends on the spatial distribution of the molecular orbitals formed near the Fermi level of metal [27, 28].
Although the resonant tunneling model provides an intuitive understanding of the process, it is not enough to answer the above questions. Several attempts to reproduce IETS spectra were performed by theorists [29–32], they provided the details of the underlying mechanism. Lorente et al. pointed out the importance of the contribution from not only the inelastic component but also the elastic component including the process that the electron emits and re-absorbs the virtual vibration as illustrated in Fig. 2.8 [29]. They carried out the density functional theory calculations of the vibrational IET process of acetylene on Cu(100) and calculated elastic and inelastic components based on a many-body generalization of the Tersoff-Hamann theory. The results explained why only the C–H stretch mode could be observed in the STM-IETS. Ueba and his co-workers presented a description of STM-IETS signal using the Keldysh Green’s function method for the molecule-induced resonance model. The elastic and inelastic tunneling currents are derived on the basis of the Anderson Hamiltonian coupled to a vibrational degree of freedom where effects of vibrational damping rate on the inelastic current were taken into consideration [31, 32].

The important finding of the theoretical efforts is that the modification of the elastic component always gives a reduction of tunneling current, while the inelastic contribution gives an increase. In summary, the total change of tunneling current is determined by the competition between the variations of elastic and inelastic components, and a vibration mode in which the elastic or inelastic component sufficiently overcome another contribution can be observed (Fig. 2.8b). These approaches explained why only limited vibrational modes are detected in the STM-IETS, e.g., only C–H (C–D) stretch mode for C\(_2\)H\(_2\). The competition between the negative elastic and positive inelastic components can also lead to even negative conductance change. Such a decrease in conductance is predicted when a molecular
state is resonant with the Fermi energy [33]. In fact, the decrease of the total current was observed in a single oxygen molecule adsorbed on Ag(110) [34, 35].

The spectral shape of IETS is of importance in understanding elementary processes of a vibrational excitation/de-excitation of adsorbates [36]. However it is not straightforward to estimate the vibration broadening, which includes fundamental properties of vibration, like lifetime and dissipation processes, in STM-IETS. Lauhon and Ho systematically studied the effect of temperature and the bias modulation on the vibrational peak width, intensity and line shape for the C–H stretch mode of a single acetylene molecule on Cu(001) [37]. They concluded that the IETS spectra are less influenced by vibrational damping because of the use of large bias modulation than the vibrational broadening. This may suppress the intrinsic features in the IETS spectra.

The selection rule of vibrational spectroscopy is important and useful to understand the molecular structure and orientation on surfaces. Several attempts to elucidate the selection rule were carried out from both of theoretical [33, 38] and experimental [39] aspects. Although a rigorous selection rule of the STM-IETS is still open question, Troisi and Ratner [40], and Paulsson et al. [33] proposed propensity rules that give useful insights to the geometric and electronic structure of nano-scale junctions containing atomic wires or molecules. Troisi and Ratner calculated the IETS signal of the junction in which two electric leads are bridged by molecules. After that, Paulsson extended the model to the unified description for electron transport systems within nano-junctions including an STM configuration. Figure 2.9 shows a phase diagram of the conductance change at a vibrational excitation. Here it is assumed that a single electronic level (\(e_0\)) is coupled with two electric leads and a localized vibration (one-level model). The phase diagram is characterized by the symmetric factor \(\alpha\) (vertical axis) and the transmission probability \(\tau\) of electron in Landauer model (transverse axis). The crossover from a decrease to an increase (boundary depicted dashed line) stems from crossing the resonance. For this model the maximal transition corresponds to the on-resonance case, which given by \(\tau_{\text{max}} = 4\alpha/(1 + \alpha)\). The symmetric factor is the ratio of the coupling between the two electric leads (\(\Gamma_{R/L}\)). The asymmetric configuration of STM junction gives \(\alpha \approx 0\) while the symmetric junction bridged by a molecule (molecular wire) \(\alpha \approx 1\). On the other hand, very low \(\tau\) is expected in the STM and molecular wires, while atomic wire exhibit \(\tau \approx 1\). The propensity rule can be examined using the extensive DFT calculations as described in Ref. [33].

For STM-IETS measurement, the high stability of STM and low extrinsic noise level of the experimental setup are required, which was the main obstacle to realize STM-IETS. Since the measurement relies on the lock-in technique, it takes a few minutes to obtain one \(d^2I/dV^2\) spectrum and the feedback loop keeping \(z\) position of the STM tip is needed to be opened during the bias sweep. The relative distance between the STM tip and adsorbate must be maintained to be constant to obtain a correct signal. As described in Sect. 2.2.2, a displacement between the tip and adsorbate causes a significant variation in tunneling current even if it is very small, which suppresses the vibrational signal from the adsorbate. To minimize this displacement (mainly caused by thermal drift) and thermal broadening of a molecular
vibration, a cryogenic condition is usually requested. Additionally, adsorbates have to be stationary under the STM tip during the measurement. When a molecule motion is induced by thermal activation or the excitation of a particular vibrational mode with tunneling electron, it becomes difficult to measure STM-IETS. However the latter phenomena can be used as an alternative vibrational spectroscopy of STM, which is discussed in the next section.

2.2.5 STM-Induced Motion and Reaction of Adsorbates

Tunneling electrons from STM can be used to induce motions and reactions of individual adsorbates. Several kinds of molecular motions and reactions have been characterized at the single molecule level in the past decade. The trailblazing works were reported by Stipe, Rezaei, and Ho in the late 1990s [41–43]. They induced and imaged of a rotation and dissociation of single oxygen molecules adsorbed on a Pt(111) surface. The mechanism was rationalized by intramolecular vibrational excitations via resonant inelastic electron tunneling. Since their pioneering efforts, various kinds of single-molecule reactions, e.g., desorption of ammonia molecule [44], bond-selective reaction of ammonia molecule [45–47], deprotonation of acetylene, benzene [48, 49] and trans-2-butene molecule [50, 51], conformational switching of porphyrin-based molecule [52] have been reported. After these findings, Kawai and her co-workers at RIKEN introduced a new concept of vibrational spectroscopy with STM, the so-called inelastic electron tunneling action spectroscopy (IET-AS) or STM action spectroscopy (STM-AS) [53]. They measured the reaction yield of a vibrationally induced the configurational change of cis-2-butene on Pd(110) as a function of applied bias voltage [Fig. 2.10]. It was found that rapid increases of reaction yield were directly related to the energy of vibrational modes of cis-2-butene. In most cases the reaction yield
The rate is increased by a factor of 10-100 after a specific mode excitation. Interestingly, the STM-AS of cis-2-butene showed the excitation of $\nu$(M-C), $\delta$(CH$_3$), $\nu$(C-C), and $\nu$(C-H) modes but only $\nu$(M-C) and $\nu$(C-H) are detected in the STM-IETS. Therefore the STM-AS can be considered as a complementary method of the STM-IETS to conduct the chemical identification with the STM. The STM-AS is applied to identify several chemical adsorbates [54–63]. More recently, the practical method to extract vibrational information from the STM-AS was developed by Motobayashi et al. [64] at RIKEN, which can be generally applied to vibrationally mediated motions and/or reactions of adsorbates. The experimental techniques to obtain the rates of reaction and motion of a single molecule are mentioned in next chapter.

I now turn to the mechanism of STM-induced motions and reactions. The process resulting in the molecular motion or reaction can be classified into the direct and indirect process. The direct process is quite simple where tunneling electron from STM excites a vibration mode that is directly associated with the coordinate of a motion or reaction. In this case we need to consider a simple vibration ladder climbing model as shown in Fig. 2.11a. The questions are the barrier height $E_B$ and the number of vibrational levels in the potential well, which can be determined by investigating the number of electrons, $n$, required inducing the motion or reaction. The rate is given by the so-called power law, $R \propto I^n$, here $I$ is the tunneling current. If a tunneling electron has enough energy to overcome the barrier, the process proceeds with one-electron ($n = 1$; solid arrow). On the other hand, if the energy is not sufficient, multiple electrons are required to overcome the barrier (dashed arrows). The direct process was observed in Xe atom switching between a tip and a Ni(110) surface [65] and the dissociation of single oxygen molecules on a Pt(111) surface [41]. The power law dependence of $R \propto$...
4.9±0.2 was found for the Xe switching, suggesting that the transfer of the Xe atom takes place through over-barrier process and the stepwise climbing of a vibrational ladder of the Xe-surface bond excitation is involved. The theoretical description of the direct process was reported by Walkup et al. [66] and Gao et al. [67]. The switching was described as the energy barrier climbing process between two potential wells modeled by truncated harmonic oscillators, where the higher vibrational states are populated by the excitation of tunneling electrons. On the other hand, for O\textsubscript{2} molecule dissociation on a Pt(111) surface, it was revealed a power low dependence of \( N \sim 1, 2, \) and 3 for the applied voltage of 0.4, 0.3, and 0.2 V, respectively. The excitation of the O–O stretching (\( \hbar \Omega = 87 \text{ meV} \)) is associated with the dissociation and the potential barrier of 0.35–0.38 eV with 5 vibrational levels in the well was calculated using a truncated harmonic oscillator. Thus, the coherent multiple jump of vibrational ladders in a one-electron scattering dominates the dissociation at 0.4 V to overcome the barrier, while the step-by-step ladder climbing through two (three)-electron process makes it possible to break the O–O bond at 0.3 (0.2) V.

On the other hand, if the motion or reaction of adsorbates is triggered by the mode that is not directly coupled with its coordinate (indirect process), the intramolecular energy transfer have to be taken into account. This indirect process was discovered in the rotation of oxygen and acetylene molecule [42, 43]. For instance, the threshold energy to induce the rotation of acetylene molecule on Cu(100) coincides with the C–H stretch excitation [43]. Obviously the C–H stretch mode is not the reaction coordinate of the rotation of acetylene. The mechanism was rationalized by the intramolecular energy transfer via anharmonic coupling between the high and low frequency modes. We now consider the fate of a molecular vibration excited via IET process. After the excitation, the excited state rapidly damps to the ground state via intramolecular energy transfer, surface phonon excitation, or electron–hole-pair (EHP) excitations on a time scale of femtosecond to picosecond. Among them the intramolecular energy transfer can eventually causes the molecular motions and reactions. Figure 2.11b illustrates the concept of the intramolecular energy transfer. When a high frequency (HF) mode is excited via IET process, its energy relaxes to a lower frequency modes associated with

![Fig. 2.11 Schematic illustration of the energy diagram of a direct and b indirect process](image-url)
with a specific reaction coordinate (RC mode) via anharmonic coupling. If a sufficient energy to surmount the barrier is accumulated in the reaction coordinate, the motion or reaction takes place. This mechanism was clearly demonstrated in the lateral hopping of carbon monoxide (CO) molecules adsorbed on a Pd(110) surface by Komeda et al. \[68\]. They showed a quantitative description of the anharmonic coupling between the HF and RC modes. Their results highlighted microscopic processes of the intramolecular energy transfer within single molecules adsorbed on metal surfaces. It was found the motion or reaction rate of indirect process also follows the power low \[42\]. Ueba et al. developed a theory quantifying elementary processes of adsorbate motions induced via intermolecular mode coupling \[69\], where they discussed one- and two-electron processes for IET-induced motions based on rate equations describing the evolution of a vibrational population of an HF mode and of an RC mode. They discussed the reaction rate in terms of inelastic tunneling rates, vibrational relaxation rates, and intermode anharmonic coupling rates. Figure 2.12 shows the proposed model for one-electron process, where anharmonic mode coupling between the HF mode (excited by tunneling electron) and the RC mode results in the excitation of the RC mode to a level above \(E_B\). For one-electron process the vibrational energy of HF mode \(\hbar \Omega\) is larger than \(E_B\). In the model of Fig. 2.12 the reaction rate \(R_{RC}\) can be obtained as

\[
R_{RC} = \frac{\tau_v}{\tau_{v,RC}} \eta_v I
\]  

(2.14)

where \(\tau_v/\tau_{v,RC}\) is the ratio of the excitation rate of the RC mode above the potential barrier \(E_B(\ll \hbar \Omega)\), and the decay rate of the \(v\) mode into low-energy excitations in the substrate (EHP excitations and bulk phonons), \(\eta_v\) and \(I\) are the inelastic-tunneling fraction and the tunneling current, respectively. The calculation of \(\tau_{v,RC}\) depends on the model of anharmonic coupling between the HF and RC modes. In the case of a CO hopping on Pd(110) the HF mode (C–O stretch) is transferred.
to transnational or rotational energy along the reaction coordinate, in competition with the fast vibrational relaxation through EHP excitation, gives

$$\frac{1}{\tau_{v,RC}} \approx \frac{1}{\tau_v} \left( \frac{\hbar \delta \omega}{E_B} \right)^{3/2} e^{-2a}$$  \hspace{1cm} (2.15)

\(\delta \omega\) represents the anharmonic coupling between the HF and RC modes, and \(\chi = \frac{E_B}{\hbar \omega}\). This theory agrees in the order of magnitude with the experimental result of a CO hopping rate on Pd(110). It is noted that this theory could explain why CO hopping is not observed on Cu(110) on contrast to Pd(110), which follows from the small \(\delta \omega\) and large \(\chi\) [68–70].

In short STM-AS provides elementary processes of adsorbate motions and reactions as well as fruitful information about vibrational excitations. Two different mechanisms have been characterized: i) direct process in which the reaction coordinate mode is directly excited by tunneling electrons, ii) indirect process that involves energy transfer between vibrational modes via anharmonic coupling.

I focused on the vibrational mediated reactions of adsorbates. However, the reactions can be also induced by electronic excitation or electron (hole) attachment with STM, which takes place at the bias voltage higher than \(\sim 1\) eV [71–74]. The electronic excitation occurs when tunneling electrons couple with electronic states of the atoms or molecule.

STM can induce and image a variety of fascinating phenomena at the single molecule level. Proper understanding of current-driven events in STM junctions is particular interest in molecular-scale electronics because it is directly related to the conductivity, heating and current-induced failure. From a theoretical perspective, current-driven dynamics in STM junctions includes the challenging subjects to describe non-equilibrium and non-adiabatic phenomena under the bias voltage and the dissipative effects of the electrodes.

### 2.2.6 Single Atom and Molecule Manipulation

An important application of tip-adsorbate interaction is the manipulation of single atoms and molecules on surfaces, which offers a precise positioning of individual adsorbates and assembly of nano-scale structures at the spatial limit. The interaction between the adsorbate and the surface is also important in the STM manipulation as well as the force working between the tip and the adsorbate. While a strong adsorbate–surface interaction makes the manipulation impossible, a weak interaction results in an uncontrollable situation.

The first example of the atom manipulation was reported by Eigler and Schweizer in 1990 [75]. They transferred Xe atoms back and forth reversibly between the tip and the surface and positioned them in fully controlled fashion on a Ni(110) surface. Figure 2.13a shows a schematic illustration of this manipulation that is called “vertical manipulation”. It is also found that single atoms can be
moved along predetermined paths of an STM tip [76]. This process is illustrated in Fig. 2.13b, which is called “lateral manipulation”. Since the proximity of an STM tip causes the strong field, the tip gives a finite force on an adsorbate [77]. This force involves both van der Waals and electrostatic contributions, which can be adjusted by controlling the tip-surface separation and the bias voltage. Bartels, Meyer and Rieder clearly demonstrated several kinds of lateral manipulation modes depending on tunneling parameters [78]. The lateral manipulation also applied to large molecules including molecular machines [79–82].

Understanding the force acting between the tip and the adsorbate is fundamental importance in STM manipulations. However it is quite hard to measure the force in STM. Recently, Ternes et al. measured the vertical and lateral forces exerted on individual adsorbed atoms or molecules by the tip [83]. They detected such forces using the simultaneous operation of STM and atomic force microscope (AFM). It was found that the force moving cobalt (Co) on Pt(111) and Co on Cu(111) required a lateral force of 210 and 17 pN, respectively. The emergence of STM/AFM paves a way to understanding the driving mechanism.

Although the STM manipulation has been well established so far, AFM can also be used for the manipulation single atoms and molecules. Recent progress of the non-contact AFM enables to manipulate atoms at semiconducting surfaces [84], even at room temperature [85, 86].

Even though the construction of nano-scale structure using STM manipulation is inherently quite slow process, it gives fascinating opportunities to investigate physical and chemical processes in desirable model systems at the single atom/molecule limit.
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