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Theory of the excitation of the vibrational mode of an adatom-substrate system under a resonant laser field

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We present a theoretical description of the excitation of a stretch mode and energy transfers among different degrees of freedom within an adatom-substrate system under an infrared resonant laser field. There are two competing mechanisms via which the adatom-substrate bond can be highly excited: The pooling process and the absorption of multiphotons. We show that if the frequency dispersion of the laser is much smaller than the anharmonicity of the selected mode, namely, if the laser can be treated as monochromatic, the pooling process is dominant in exciting the stretch mode to highly vibrational states. As the frequency dispersion of the laser increases, the excitation to highly vibrational states by direct photon absorption becomes more dominant. We further show that the dependences of the two mechanisms on photon frequency are quite different: If pooling dominates, there is only a single peak in the excitation probability; if multiphoton absorption dominates, there may exist several peaks and the main peak may exhibit a redshift. These findings are illustrated using the H/Si(111) system as a prototype example.

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I. INTRODUCTION

Laser has been widely used in surface science. It can be used to investigate the vibrational spectroscopy of the normal modes of adsorbates to reveal the chemical and structural information at surfaces.[1] It can also provide valuable information about the interadsorbate interaction and the adsorbate-substrate coupling.[2] However, it has not been very successful in using laser to achieve selective vibrational excitation at surfaces,[3] though selective excitation enjoys great success with molecules in the gas phase.[4] The main reason is that the substrate in a surface system has many low-frequency phonon modes that can smear out the selectivity. This is in stark contrast with gas-phase molecules, which have few low-frequency phonons.

To achieve selective excitation at surfaces, two conditions have to be met. First, the vibrational mode of the adatom-substrate bond should have a long lifetime. In other words, the vibrational mode should not be strongly coupled to the substrate phonons. Second, the substrate should be transparent to the applied laser so that the laser generates little heat in the substrate. It was pointed out in Ref. 5 that these conditions are met for the H/Si(111) system. Therefore, an infrared laser can be used to selectively excite the Si-H bonds, potentially offering a way to control silicon film growth.[5] Recently, the desorption of hydrogen from the Si(111) surface by resonant excitation of the Si-H vibrational stretch mode has been reported.[6] These developments thus urge a more in-depth study of selective excitation at surface.

In this paper, we study the mechanisms via which the stretch mode of the adatom-substrate bond is excited to highly vibrational states in an adatom-substrate system where the selective excitation is achievable. We will focus on the excitation to the second excited state. Discussions of higher excited states are similar.

The frequency of the stretch mode is typically high; we consider only the temperature range where its thermal excitation can be neglected. In this case, the stretch mode can achieve the second excited state by either direct photon absorption or pooling. These mechanisms are illustrated in Fig. 1.

There are two kinds of photon absorption. One is called one-by-one process, where the adatom-substrate bond absorbs one photon at a time. The other is multiphoton absorption, where two or more photons are absorbed simultaneously. Because of the large anharmonicity $U=\omega_{01}-\omega_{12}>0$ in the stretch mode of an adatom-substrate system, the photon absorption to higher excited states is always a nonresonant process. The larger the anharmonicity is, the smaller is the excitation probability. In practice, this anharmonicity is overcome by using short-pulsed laser that is usually picosecond or even femtosecond long. In the one-by-one process, because of the rapid phase relaxation (always picosecond long), the process is incoherent. Therefore, we can treat each

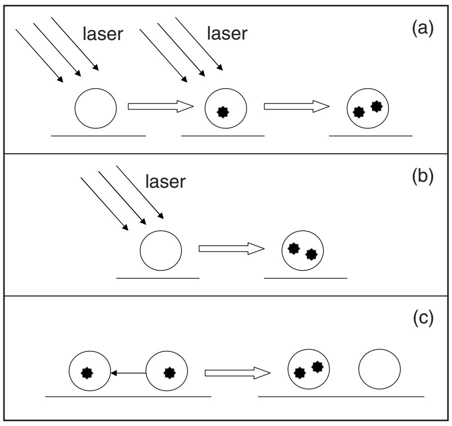

FIG. 1. Illustration of different excitation mechanisms to highly excited states of the adatom-substrate bond: (a) one-by-one photon absorption, (b) simultaneous multiphoton absorption, and (c) pooling process. The dot indicates how highly the adatom is excited.

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absorption independently. For the one-by-one process to dominate, the lifetime of the first excited state has to be relatively long. As the laser intensity increases, the nonlinear multiphoton absorption will become more important.

The excitation to the second excited state can also be induced by vibrational energy pooling through the lateral interaction of the neighboring bonds. Chang and Ewing[7] reported the observation of this effect in the CO/NaCl system, where dipole coupling induces many CO molecules, each of which is excited by a single photon, to pool their energy into a few CO molecules so that these molecules are highly excited. Because of the anharmonicity, pooling is an energy downward process, which is energetically preferred.

The purpose of this paper is to examine these mechanisms in detail. We first discuss these excitation mechanisms independently and then compute the probability of each mechanism with a set of master equations. A critical assumption in our work is that each of the adatom-substrate bonds of the system can be regarded as containing a specific number of vibrational quanta. The assumption is valid whenever the time scale for energy transfer is much longer than the dephasing time. Although the bonds are excited collectively by the laser, it is reasonable to assume that the collective behavior is destroyed by the rapid dephasing and the time scale of the energy localization is much shorter than that of other processes. In our study, we use the H/Si system as an example to illustrate the results for three reasons: (1) this system is simple and thus is an ideal prototype system for such illustrations; (2) the previous studies show that selective excitation does exist in this system;[5,6] and (3) this system is technologically important.[6]

We find that if the frequency dispersion of the laser is much smaller than the anharmonicity of the selected mode, the pooling process is dominant. As the frequency dispersion of the laser increases, multiphoton absorption becomes more dominant. We also find that the frequency dependences of the two mechanisms are quite different: If pooling dominates, there is only a single peak; if multiphoton absorption dominates, there may exist several peaks and the main peak may exhibit a redshift.

The paper is organized as follows: In Sec. II, we present a general theoretical description of the system and discuss the computation of the stretch mode and dipole moment. In Sec. III, we study the photon-absorption processes, including both one-photon absorption and two-photon simultaneous absorption. In Sec. IV, we investigate the energy transfers between neighboring adatom-substrate bonds, which include resonant transfer and pooling process. A short discussion about the lifetime of the stretch mode is given as well. In Sec. V we set up the master equations and compute the probability of the excitation induced by each mechanism. Both monochromatic and short-pulsed lasers are considered. Finally, a summary is given in Sec. VI.

II. GENERAL DESCRIPTION

We consider a group of atoms which are adsorbed on an insulating substrate with a submonolayer coverage. We wish to know how the stretch mode of adatom-substrate bonds can be excited to high excitation states when the system is illuminated by a resonant infrared laser. This kind of excitation is the result of various energy-transfer processes in the system. First, there are energy transfers from the laser to adatoms or the substrate via photon absorption. Second, energy can be transferred between neighboring adatom-substrate bonds. Third, excited adatoms can dissipate energy into the substrate and relax to the ground state or vice versa. We will focus on the first two processes as the third process is well understood.

Together, the above prescribes a very complicated many-body system. To make it tractable, we introduce a few reasonable assumptions. First, we assume the absence of electronic excitations since only an infrared laser is used. Second, the adatom and the substrate form a chemical bond and thus the adatoms are spatially well localized. Third, the substrates are regarded as a collection of phonons and these phonons are coupled weakly to the vibrational modes of the adatom-substrate bond. With these assumptions, we write the system Hamiltonian as

$$\mathcal{H} = \sum_i \left[\frac{P_i^2}{2m^*} + V(\vec{r}_i) \right] + \sum_{i,j} U_{i,j} - \sum_i \mathbf{D}_i \cdot \mathbf{E}_i + H_B + H' , \tag{1}$$

where $V(\vec{r}_i)$ is the potential describing the adatom-substrate bond at the ith site and $U_{i,j}$ is the lateral interaction between adatoms. The laser field is treated as a classical field $\mathbf{E}$ and is coupled to the electric dipole moment $\mathbf{D}$ of the adatom. H_B represents the substrate phonons and the last term H' describes the coupling between the stretch bond and the substrate phonons.

A. Stretch mode of the adatom-substrate bond

We first focus on an adsorbed atom at the ith site of the substrate. The Hamiltonian for this adatom is

$$H_i = -\frac{\hbar^2}{2m^*}\nabla_i^2 + V_i(\vec{r}), \tag{2}$$

where m^* is the effective mass and $V_i(\vec{r})$ is the interaction potential between the adatom and the substrate. If the substrate surface is isotopic, i.e., there is an azimuthal symmetry, V can be written as

$$V = V(z) + V(R) + W(z,R), \tag{3}$$

where z and R represent the motions of the adatom normal and parallel to the substrate surface, namely, the stretch and bending modes, respectively. W is the coupling between the two modes. For the H/Si(111) and H/Si(100) systems, W can be omitted when only the low-lying states are considered.[8,9] The simplest treatment of $V(z)$ and $V(R)$ is the harmonic approximation. However, for the stretch mode, the anharmonicity is generally strong and the harmonic approximation is insufficient. A better choice is the Morse potential $V(z) = D(e^{-2\alpha z} - 2e^{-\alpha z})$, where D is the dissociation energy and α is a parameter determining the anharmonicity. Since the anharmonicity is constant in the Morse potential but it is not in reality, the Morse potential is a good approximation only for the lowly excited states.

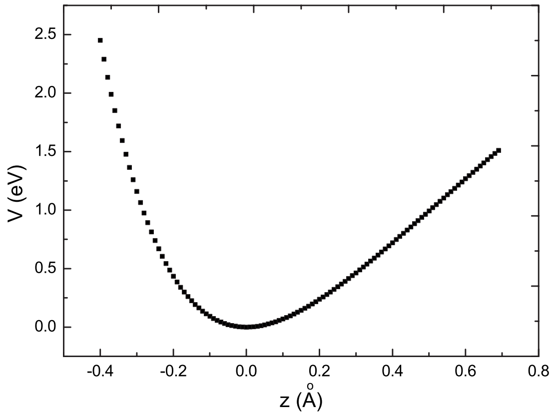

FIG. 2. The normal potential $V(z)$ for the Si-H bond on the Si(111) surface. The equilibrium position is taken at $z=0$.

A better way is to compute the normal potential $V(z)$ with *ab initio* calculations without any fitting parameter. We use the H/Si(111) system as an example to illustrate this method. The calculation is implemented by the *ab initio* code VASP.[10] The Perdew-Wang (PW91) (Ref. 11) exchange-correlation functional has been used and the inner electrons are replaced by projector augmented wave (PAW) pseudopotentials.[12] The energy cutoff is 300 eV. The supercell contains six-layer Si slabs with a vacuum of 13 Å. For a 3×3 surface cell, a Monkhorst-Pack grid with $4\times4\times1$ k points is used. Since silicon is much heavier than hydrogen, the stretch mode is primarily localized on the hydrogen atom. Therefore, in our *ab initio* calculations we keep all the silicon atoms fixed (frozen phonon calculation) and elongate/shorten one Si-H bond. To map out the potential, we take 110 equally spaced points for the hydrogen atom along the z direction from -0.4 to 0.7 Å away from the equilibrium position. The results are shown in Fig. 2. These data are enough to ensure the accuracy of the lowest few excited states. With these data, we solve numerically the following one-dimensional (1D) Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2}+V(z)\right]\psi(z)=E\psi(z), \tag{4}$$

where the effective mass is given by $m^*=\frac{m_{\mathrm{H}}m_{\mathrm{Si}}}{m_{\mathrm{H}}+m_{\mathrm{Si}}}$. We find that the frequency of the Si-H stretch mode is 2025 cm^{-1} and the anharmonic frequency is 75 cm^{-1}, which are in good agreement with other theoretical calculations.[13–15] However, this computed stretch mode frequency is 58 cm^{-1} smaller than the experimental result (2083 cm^{-1}).[16] There are several possible reasons for this difference: (1) The frozen phonon calculation causes 1% error.[13] (2) In our calculations, we omitted the interaction of the adatom with other adatoms and the substrate phonons. This may also induce a frequency shift.[17,18] (3) The effective mass m^* is an approximation. Our computed anharmonicity frequency is 15 cm^{-1} smaller than the experimental one (90 cm^{-1}), which is related to the existence of the two-phonon bound state.[16] Since the lateral interaction between the adatoms is ignored here, the two-phonon bound state is not taken into account.

B. Lateral interaction between the adatoms and the dipole moment

As discussed above, the adatom-substrate bonds are well localized. In this case, the lateral interaction between the adatoms is mainly via dipole coupling, which is true for the H/Si system.[16] The dipolar interaction is described by

$$U_{i,j}=\frac{\mathbf{D}_i\cdot\mathbf{D}_j}{4\pi\varepsilon_0|\mathbf{R}_i-\mathbf{R}_j|^3}, \tag{5}$$

where $\mathbf{R}_i$ is the coordination of the ith site of the substrate. Because the substrate atoms vibrate around the equilibrium positions, we have $\mathbf{R}_i=\mathbf{R}_{i0}+\mathbf{r}_i$, where $\mathbf{R}_{i0}$ is the equilibrium position and $\mathbf{r}_i$ is a small displacement. We expand Eq. (5) around the equilibrium positions to the first order:

$$U_{i,j}=\frac{\mathbf{D}_i\cdot\mathbf{D}_j}{4\pi\varepsilon_0R_0^3}-\frac{3\mathbf{D}_i\cdot\mathbf{D}_j}{4\pi\varepsilon_0R_0^5}(\mathbf{r}_i-\mathbf{r}_j)\cdot\mathbf{R}_0. \tag{6}$$

Since $\mathbf{r}_i$ represents the motion of the substrate atom, the first-order term in the above equation actually represents a coupling of the adatoms to the substrate phonons. Because the lateral interaction decays with distance with the inverse cubic law, we consider only the coupling between nearest neighboring adatoms.

The dipole moment $\mathbf{D}_i$ is generally a vector. In our discussion, we focus on the case where only the stretch mode is important. In this case, only the component perpendicular to the surface $D(z)$ is significant. Consequently, the dipole moment can be regarded as a scalar with its direction represented by the sign of $D(z)$. A simple model of the dipole is $D(z)=D_0+\alpha z$, where D_0 is the polarization of the bond at equilibrium and $\alpha=\frac{dD(z)}{dz}\big|_{z_0=0}$ is a constant. The model is good if z is not far away from the equilibrium position. When the vibrational amplitude is large and the nonlinearity is strong, a Mecke-type function is preferred,[8,19]

$$D(z)=A_0+A_1z^me^{-A_2z}, \tag{7}$$

where A_0,A_1,A_2,m are system parameters and can be determined by fitting the *ab initio* results or the experimental data. In this paper, we have performed a frozen phonon *ab initio* calculation to get the dipole moment $D(z)$ of the H/Si system. The method is the same as for the potential calculation presented before (Fig. 2). The result is shown in Fig. 3. In these calculations, only one Si-H bond is allowed to elongate or shorten, and due to the symmetry of the supercell, the dipole moment at the equilibrium position is zero.

In the following discussions, what is needed in computation is the dipolar matrix elements of the vibrational stretch modes, $D_{mn}=\langle m|D(z)|n\rangle$. For H/Si(111), we have $D_{01}=0.016\,53$ eÅ and $D_{12}=0.024\,78$ eÅ.

III. PHOTON ABSORPTION

When an infrared laser is applied to an adatom-substrate system, the photons can be absorbed by either adatoms or the substrate. If the photons are absorbed by the substrate, the substrate will be heated up and eventually excite the adatoms. This process is almost identical to directly increasing

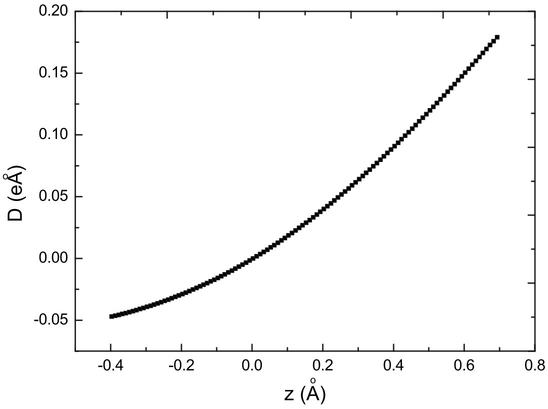

FIG. 3. The normal dipole moment $D(z)$ of the Si-H bond on the Si(111) surface.

the substrate temperature and is less intriguing. In this paper, we focus on the system where the laser is transparent to the substrate so that the direct laser heating of the substrate is minimal.

When the laser frequency is tuned to the vibrational mode of the adatoms, the adatoms can absorb photons and jump to excited states. The dominant process is one-photon absorption, in which the adatom absorbs one photon and is excited from the ground state to the first excited state. Other processes are also possible, for example, one-by-one absorption and multiphoton absorption (Fig. 1). In one-by-one absorption, the adatom is excited to the second excited state by absorbing two photons one after another. In the multiphoton process, the adatom is excited to highly excited states by absorbing two or more photons at the same time. We investigate the probability of these different photon-absorption processes.

As the interactions among the adatoms and the substrate are not important in the absorption of photons, we ignore them and study the following one-body Hamiltonian:

$$H = H_i - \boldsymbol{D}_i \cdot \boldsymbol{E}_i, \tag{8}$$

which is the Hamiltonian of the adatom on the ith site. The interaction between the adatom and the laser is described within the semiclassical electric dipole approximation and the infrared laser is represented by its electric field,

$$\boldsymbol{E}_i = \boldsymbol{E}_0 \cos \omega t, \tag{9}$$

where $\boldsymbol{E}_0$ is independent of the position as the spatial scale of an atom is much smaller than the wavelength of the infrared laser. For simplicity, we omit the subscript i below. When the polarization of the electric field is along the z direction, the Hamiltonian can be rewritten as

$$H = H_0 - D(z)E_0 \cos(\omega t), \tag{10}$$

where H_0 is the Hamiltonian of a single oscillator described above.

A. One-photon absorption

For the one-photon absorption $|0\rangle \to |1\rangle$, according to time-dependent perturbation theory, the transition possibility at time t is given by

$$P_{01}(t) = \frac{|D_{01}|^2 E_0^2}{4\hbar^2} \frac{\sin^2[(\omega_{01} - \omega)t/2]}{[(\omega_{01} - \omega)/2]^2}, \tag{11}$$

where $\omega_{01} = \omega_1 - \omega_0$ is the frequency of the stretch mode. When t is long enough, only the resonant photon, i.e., $\omega = \omega_{01}$, can be absorbed:

$$\begin{aligned} P_{01}(t \to \infty) &= \frac{\pi t}{4\hbar^2} |D_{01}|^2 E_0^2 \delta[(\omega_{01} - \omega)/2] \\ &= \frac{\pi t}{2\hbar^2} |D_{01}|^2 E_0^2 \delta(\omega_{01} - \omega). \end{aligned} \tag{12}$$

The transition rate is given by

$$w_{01} = \frac{d}{dt} P_{01}(t) = \frac{\pi}{2\hbar^2} |D_{01}|^2 E_0^2 \delta(\omega_{01} - \omega). \tag{13}$$

For a real system, the line shape of the absorption peak is broadened and has a finite full width at half maximum (FWHM). We replace the δ function by a Lorentzian with FWHM of 2γ,

$$L(\omega) = \frac{\gamma}{\pi[(\omega_{01} - \omega)^2 + \gamma^2]}. \tag{14}$$

The transition rate consequently becomes

$$w_{01} = \frac{1}{2\hbar^2} |D_{01}|^2 E_0^2 \frac{\gamma}{(\omega_{01} - \omega)^2 + \gamma^2}. \tag{15}$$

The transition rate w_{10} for $|1\rangle \to |0\rangle$ is identical, $w_{10} = w_{01}$.

The cross section is defined as the effective area of the adatom that absorbs a photon:

$$\sigma = w_{01}/F, \tag{16}$$

where F is the photon flux, defined as the number of photons arriving at the surface in unit area per second. Notice that the flux F satisfies the relation

$$F\hbar\omega = \varepsilon_0 E_0^2 c/2, \tag{17}$$

where c is the speed of light and ε_0 is the dielectric constant of vacuum. Substituting Eqs. (15) and (17) into Eq. (16) and setting $\omega = \omega_{01}$ for resonance, we get

$$\sigma = \frac{|D_{01}|^2 \omega}{\hbar \varepsilon_0 c \gamma}. \tag{18}$$

For H/Si(111), $2\gamma = 1\ \text{cm}^{-1}$,[17,20] $\omega = 2083\ \text{cm}^{-1}$,[16] and D_{01} can be calculated by the *ab initio* result in Sec. II. The result is $\sigma \approx 10^{-17}\ \text{cm}^2$, which is in agreement with the estimate from the experimental studies.[5]

When the time spread of the laser pulse is longer than the dephasing time, the excited state becomes incoherent with the laser and the first excited state can be excited to the second excited state incoherently. Because of the anharmonicity of the oscillator, the $|1\rangle \to |2\rangle$ transition is off-resonance if $\omega = \omega_{01}$. Since the absorption peak has a finite linewidth, the nonresonant process has a small transition rate,

$$w_{12} = \frac{1}{2\hbar^2} |D_{12}|^2 E_0^2 \frac{\gamma}{(\omega_{12} - \omega_{01})^2 + \gamma^2}. \tag{19}$$

In the above discussion, we have not considered the coupling with the substrate. If the absorption is off-resonance, the system can absorb a photon by creating a stretch mode phonon and transferring the anharmonic energy to the substrate. As will be shown in Sec. IV B, this energy transfer is mainly due to the inelastic scattering with a substrate phonon at room temperature. For simplicity, we assume the stretch mode is strongly coupled to a localized phonon which dominates the dephasing. The discussion here follows Ref. 17. The Hamiltonian is given by

$$H = H_0 + H_B - \boldsymbol{D} \cdot \boldsymbol{E} + \delta\omega \hat{n} B^{\dagger} B, \tag{20}$$

where $\hat{n}$ is the phonon number operator of the stretch mode, B and $B^{\dagger}$ are the creation and annihilation operators for a quasilocalized surface mode, respectively, and $\delta\omega$ is the strength of the coupling. Using the second-order perturbation theory, we can get

$$w(n) = \frac{2\pi}{\hbar^4}\frac{E_0^2}{4}\left|\frac{\langle n+1|D|n\rangle}{U}\right|^2 \delta\omega^2 \times \int d\omega d\omega' n(\omega)[n(\omega')+1]\rho(\omega)\rho(\omega')\delta(U+\omega-\omega'), \tag{21}$$

where $w(n)$ is the transition rate between the nth and $(n+1)$th excited states. We use this notation to distinguish from the transition rates without substrate phonons (w_{ij}). In the equation above, $U=\omega_{01}-\omega_{12}$ is the anharmonic frequency, $n(\omega)$ is the Bose-Einstein distribution of substrate phonons, and $\rho(\omega)$ is the local density of the states which is assumed to be a Lorentzian,

$$\rho(\omega) = \frac{\eta/2\pi}{(\omega-\omega_0)^2 + (\eta/2)^2}. \tag{22}$$

Assuming $k_BT \gg \eta, U$, we get

$$\int d\omega d\omega' n(\omega)[n(\omega')+1]\rho(\omega)\rho(\omega')\delta(U+\omega-\omega') \approx \frac{\eta/\pi}{U^2+\eta^2} n(\omega_0)[1+n(\omega_0)]. \tag{23}$$

As the linewidth of the stretch mode is given by[17,20]

$$2\gamma = 2\frac{\delta\omega^2}{\eta} e^{\hbar\omega_0/k_BT}(e^{\hbar\omega_0/k_BT}-1)^{-2}, \tag{24}$$

we obtain

$$w(n) = \frac{E_0^2}{2\hbar^2}\left|\frac{\langle n+1|D|n\rangle}{U}\right|^2 \frac{\gamma}{1+(U/\eta)^2}. \tag{25}$$

Now we compare it with Eq. (19). The ratio

$$\frac{w(n=1)}{w_{12}} = \frac{U^2+\gamma^2}{U^2+U^4/\eta^2}. \tag{26}$$

Generally $U^2/\eta \gg \gamma$; therefore, $w(n=1) < w_{12}$.

In the discussions above, we have omitted the lateral interaction of the oscillators. When the lateral interaction is involved, there exists a local field and the peak of the absorption will shift depending on the population of the excited states.[17] However, if the anharmonicity is much larger than the bandwidth of the stretch mode, it is possible to neglect the lateral coupling.[18] The two-phonon bound state has not been discussed either. A simple method to fix the problem is to replace the anharmonicity frequency U with the experimental result which includes the two-phonon bound state.

B. Multiphoton absorption

When the laser intensity is strong, the adatom-substrate bond can absorb two (or more) photons simultaneously. We focus on two-photon absorption since it is the strongest among all multiphoton-absorption processes. Because it is a higher-order process, the probability of two-photon absorption is much smaller than that of one-photon absorption. The transition probability was first derived by Göppert-Mayer[21] using the second-order perturbation theory. The second-order coefficient is given by

$$C_{02}^{(2)}(T) = \left(\frac{1}{i\hbar}\right)^2 \int_0^T dt \langle 2|E(t)\cdot D|1\rangle e^{i\omega_{21}t} \times \int_0^t dt_1 \langle 1|E(t_1)\cdot D|0\rangle e^{i\omega_{10}t_1}. \tag{27}$$

In the case of a monochromatic laser, namely, $E(t)=E_0(e^{i\omega t}+e^{-i\omega t})/2$, the coefficient becomes

$$C_{02}^{(2)}(T) = \frac{1}{4\hbar^2}E_0^2 D_{21}D_{10}\left\{\frac{1-\exp[i(\omega_{21}-\omega)T]}{(\omega_{10}-\omega)(\omega_{21}-\omega)} - \frac{1-\exp[i(\omega_{20}-2\omega)T]}{(\omega_{10}-\omega)(\omega_{20}-2\omega)}\right\}. \tag{28}$$

The probability of two-photon absorption is

$$P_{02}(t) = |C_{02}^{(2)}(t)|^2 = \frac{E_0^4 D_{10}^2 D_{21}^2}{4\hbar^4}\left[\frac{\sin^2[(\omega_{21}-\omega)t/2]}{(\omega_{21}-\omega)^2(\omega_{10}-\omega)^2} + \frac{\sin^2[(\omega_{20}-2\omega)t/2]}{(\omega_{20}-2\omega)^2(\omega_{10}-\omega)^2} - \frac{\sin^2[(\omega_{21}-\omega)t/2] + \sin^2[(\omega_{20}-2\omega)t/2] - \sin^2[(\omega_{10}-\omega)t/2]}{(\omega_{21}-\omega)(\omega_{20}-2\omega)(\omega_{10}-\omega)^2}\right]. \tag{29}$$

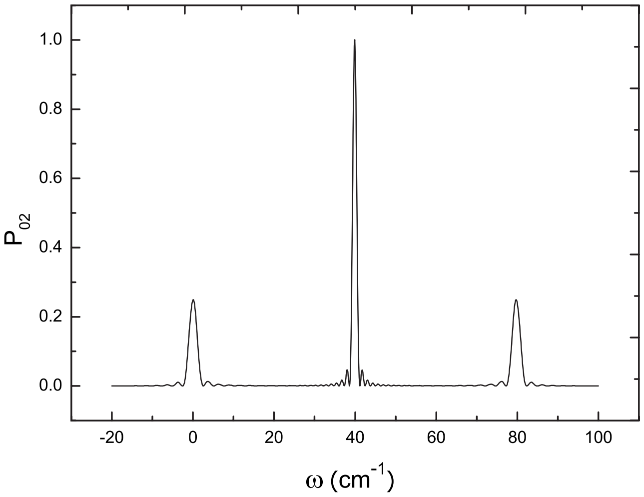

FIG. 4. Dependence of the two-photon absorption probability on the laser frequency. P_{02} is normalized to 1. The anharmonicity is 80 cm^{-1} and ω_{12} is set as the reference point.

The frequency dependence of P_{02} is shown in Fig. 4. There exist three peaks: a major one at $\omega=(\omega_{01}+\omega_{12})/2$ and two minor satellite ones at $\omega=\omega_{01},\omega_{12}$. If we consider only resonant absorption, namely, $\omega\approx\omega_{02}/2$, the absorption rate is given by

$$w_{02}=\frac{P_{02}}{t}\approx\frac{\pi E_0^4D_{10}^2D_{21}^2}{8\hbar^4(\omega_{10}-\omega)^2}\delta(\omega_{20}-2\omega). \tag{30}$$

In the above equation, we may use a Lorentzian with a linewidth $2\gamma'$ to replace the δ function for realistic computation.

IV. ENERGY TRANSFER BETWEEN THE ADATOMS

Once the adatoms are excited by laser at the surface, the acquired energy can be redistributed among adatoms due to the dipole-dipole coupling. There are two kinds of energy transfer via the stretch mode between two neighboring adatoms. One occurs when an adatom in its nth excited state of the stretch mode is excited to the $(n+1)$th excited state by acquiring a phonon from its neighbor which is in the $(n+1)$th excited state. This energy-transfer process is denoted as $|n,n+1\rangle\rightarrow|n+1,n\rangle$. Since the energy is conserved between the neighboring adatoms during the process, we call it resonant energy transfer. The other process, denoted as $|n,m\rangle\rightarrow|n-1,m+1\rangle(n\neq m+1)$, is an off-resonant energy transfer. Due to the anharmonicity, the energy is not conserved between the neighboring adatoms, and it requires energy exchange with the substrate phonon. These two fundamental processes are responsible for many physical phenomena. For example, an energy pooling can occur via the off-resonant energy transfer.[7]

A. Resonant energy transfer

When the adatom-substrate system is illuminated by an infrared laser, the adatoms can be excited by absorbing photons. It is important to know whether the excitation energy will be passed on to other adatoms during the lifetime of the excited states. For this purpose, we need to know the rate of resonant energy transfer between neighboring adatoms. Since the energy is conserved, the involvement of the substrate is minimal. As a result, the resonant energy transfer can be described by the following Hamiltonian:

$$H=H_1+H_2+\frac{D_1D_2}{4\pi\varepsilon_0R_0^3}, \tag{31}$$

where H_1 and H_2 are the Hamiltonians for the two neighboring adatoms and the third term is for the dipolar interaction between them. Since the lateral interaction is small compared to H_1 and H_2, we regard it as a perturbation.

Each adatom can be regarded as an oscillator with its eigenstates given by $|m\rangle$. When the dipolar interaction is ignored, the eigenstates of the two neighboring adatoms are given by $|m,n\rangle=|m\rangle|n\rangle$ with the corresponding eigenvalues $E_{n,m}=E_n+E_m$. When the interaction is turned on, it has two consequences: (i) the eigenenergy shifts and (ii) the degeneracy, e.g., between $|1,0\rangle$ and $|0,1\rangle$, is lifted. We focus on the latter since it is related to the resonant energy transfer. We take the $|1,0\rangle\rightarrow|0,1\rangle$ transfer as an example. After applying the degenerate perturbation theory, we obtain a 2×2 Hamiltonian matrix,

$$H=E_{10}+\frac{1}{4\pi\varepsilon_0R_0^3}\begin{pmatrix}\langle01|D_1D_2|01\rangle & \langle01|D_1D_2|10\rangle\\ \langle10|D_1D_2|01\rangle & \langle10|D_1D_2|10\rangle\end{pmatrix}. \tag{32}$$

Diagonalizing the matrix, we can get the energy split $\Delta\approx0.135$ meV, from which we will be able to find the resonant transfer frequency. Because the phonon oscillates coherently between the two adatoms, the possibility of the phonon localized in one Si-H bond is given by

$$P_{10}(t)=\cos^2\left(\frac{\Delta}{2\hbar}t\right). \tag{33}$$

However, the rapid dephasing[22] will destroy the coherent oscillation. Therefore, we define a time scale t^* for the transfer by setting $P_{10}(t^*)=1/e$.[23] The frequency of the transfer is roughly given by

$$\nu'=\frac{1}{t^*}=\frac{\Delta}{2\hbar\arccos(e^{-1/2})}=1.12\times10^{11}\ \text{s}^{-1}. \tag{34}$$

Since each Si-H bond has six neighbors, the effective transfer frequency is $\nu=6\nu'=6.74\times10^{11}$ s^{-1}. The lifetime of the Si-H first excited state is about 0.8 ns,[24] which is 3 orders of magnitude larger than the resonant transfer time. This shows that the resonant energy transfer is very frequent. Since the laser power usually has a Gaussian distribution in the cross section of the beam, it is clear that there are more Si-H bonds getting excited at the center of the laser beam. However, due to the rapid resonant energy transfer, these excitations will be spread out in a short time. As a result, it is reasonable to assume that excited adatoms (or adatom-substrate bond) are uniformly distributed in the laser-illuminated area.

B. Off-resonant energy transfer

We now turn to off-resonant energy transfer. Via this process, an interesting phenomenon called energy pooling can occur. For example, one adatom-substrate bond in its first excited state can jump to the second excited state by acquiring one phonon from its neighbor which was in the first excited state and returns to the ground state by giving out the phonon. Since there may be other excited neighbors or the de-excited bond may be excited again by resonant energy transfer from its neighbors, this newly excited adatom-substrate bond may acquire one more phonon via off-resonant energy transfer and get excited to the third excited state. This process can go on until the lifetime of the highly excited state becomes too short to allow for off-resonant energy transfer. In the CO/NaCl system, the CO stretch mode can be excited to $n=15$ by this pooling mechanism.[7] For a concrete system, the importance of the energy pooling is determined by how fast the off-resonant energy transfer can occur.

Due to the anharmonicity, the energy of the final state is lower by $\Delta E=\hbar U$ than that of the initial state, and the excess energy is dissipated to the substrate. There are a couple of ways for the substrate to absorb the energy: (1) inelastic scattering of a bulk phonon from the excited oscillator and (2) creation of a bulk phonon. The former process was studied in Ref. 17 with the assumption that the process is dominated by coupling to the substrate phonon that is largely responsible for the dephasing of the stretch mode. The interaction Hamiltonian is given by[17]

$$V=\sum_{i,j} t_{ij} b_i^\dagger b_j + \delta\omega \sum_i n_i B_i^\dagger B_i, \tag{35}$$

where t_{ij} describes the strength of the dipole coupling, $\delta\omega$ describes the coupling between the stretch mode and the substrate phonons, n_i is the phonon number operator of the ith site, and $B_i, B_i^\dagger$ are the creation and annihilation operators for a quasilocalized surface mode. Using perturbation theory, one can obtain the transfer rate,[17]

$$w_{ij}=\frac{8\pi}{\hbar}\left|\frac{t_{ij}}{U}\right|^2 \delta\omega^2 \int d\omega d\omega' n(\omega)[n(\omega')+1] \times \rho(\omega)\rho(\omega')\delta(U+\omega-\omega'), \tag{36}$$

where $n(\omega)$ is the Bose-Einstein distribution and $\rho(\omega)$ is the density of states of the local surface phonon described by

$$\rho(\omega)=\frac{\eta/2\pi}{(\omega-\omega_0)^2+(\eta/2)^2}. \tag{37}$$

After some simplifications, we find

$$w_{ij}=4\left(\frac{t_{ij}}{U}\right)^2 \frac{2\gamma}{1+(U/\eta)^2}, \tag{38}$$

where 2γ is the linewidth of the stretch mode given by Eq. (24). Since other parameters depend on temperature weakly, the transfer rate w_{ij} depends on temperature mainly via $\gamma(T)$.

For H/Si(111), the bandwidth of the stretch mode $\Delta\Omega \approx 9t_{\langle i,j\rangle}$, where $\langle i,j\rangle$ means the nearest sites. At room temperature (300 K), $2\gamma=1\ \mathrm{cm}^{-1}$, $\Delta\Omega=10\ \mathrm{cm}^{-1}$, $U=87\ \mathrm{cm}^{-1}$, and $\eta=52\ \mathrm{cm}^{-1}$, and for every bond there are six nearest neighbors. Using these parameters, we have $w=\Sigma_j w_{ij}\approx 2\times 10^8\ \mathrm{s}^{-1}$. At $T=130$ K, $2\gamma=0.1\ \mathrm{cm}^{-1}$,[20] and we obtain $w\approx 2\times 10^7\ \mathrm{s}^{-1}$, which is 1 order of magnitude smaller than that at 300 K.

For the latter process involving the creation of bulk phonons, we follow the study in Ref. 23. The coupling between the oscillator and the substrate is given by the first-order term of Eq. (6), which involves only one substrate phonon. Since the anharmonicity is always smaller than the Debye frequency of the substrate, the process needs to create only one substrate phonon and the truncation here is reasonable. With the choice of $\mathbf{R}_0$ being along the y axis, the Hamiltonian is given by

$$H=H_1(z_1)+H_2(z_2)+H_B-\frac{3D_1(z_1)D_2(z_2)}{4\pi\varepsilon_0 R_0^4}(y_1-y_2). \tag{39}$$

Here the substrate Hamiltonian H_B is chosen to be two independent collections of harmonic oscillators with frequencies ω_α,

$$H_B=\sum_\alpha \omega_\alpha (b_{1\alpha}^\dagger b_{1\alpha}+b_{2\alpha}^\dagger b_{2\alpha}). \tag{40}$$

H_B is comprised of two separate collections to allow for the definition of two collective coordinations, y_1 and y_2,

$$y_i=\sum_\alpha \left(\frac{\hbar}{2M\omega_\alpha}\right)^{1/2}(b_{i\alpha}^\dagger+b_{i\alpha}), \tag{41}$$

where M is the mass of the substrate atoms. The density of states is assumed to be of the normalized Debye form,

$$\rho(\omega)=\frac{3\omega^2}{\omega_D^3}, \quad 0\le\omega\le\omega_D, \tag{42}$$

where ω_D is the Debye frequency. According to the Fermi golden rule, the transfer rate is

$$w=\int \rho(\omega)\frac{2\pi}{\hbar^2}|V_{i,f}|^2\delta(\omega_f-\omega_i), \tag{43}$$

where we use the notation $V_{i,f}=\langle i|V|f\rangle$. After a series of calculation and simplification, the rate is given by

$$w=\frac{12\pi[n(U)+1]U}{\hbar M\omega_D^3}\left(\frac{3|D_{0,1}||D_{1,2}|}{4\pi\varepsilon_0 R_0^4}\right)^2, \tag{44}$$

where U is the anharmonic frequency, $n(U)$ is the Bose-Einstein thermal occupation number, and $D_{ij}=\langle i|D|j\rangle$. For H/Si(111), it gives $w=4.2\times 10^6\ \mathrm{s}^{-1}$. The temperature dependence of this phonon-creating process is mainly via $n(U)$. When the temperature is low, it is almost temperature independent.

We can conclude that when the temperature is high, the inelastic-scattering process dominates, whereas the phonon-creation process dominates when temperature is low. Physically this conclusion is reasonable because the coupling in the former process is stronger than that in the latter one. When the temperature is high, both processes contribute with the former one dominating. When the temperature is low enough, there are few phonons in the substrate that can scatter with the stretch mode phonon. Therefore, the former process is quenched.

In the discussions above, we calculated the $|1,1\rangle \rightarrow |0,2\rangle$ process, in which the energy is dissipated to the substrate. The calculation of the reverse process $|0,2\rangle \rightarrow |1,1\rangle$ is straightforward. To do so, we only need to replace $n(U)+1$ with $n(U)$ in Eq. (44). When the substrate is in equilibrium, we have

$$\frac{w_{11\to02}}{w_{02\to11}} = \frac{n(U)+1}{n(U)} = \exp(\hbar U/k_B T), \tag{45}$$

which is just the detailed balance relation.

C. Lifetime of the excited stretch mode

The excited stretch mode can relax by transferring energy into low-frequency modes, which include the wagging modes of the adatom-substrate bond and substrate phonons. Because the frequency of stretch mode is generally much larger than that of the other modes, the relaxation always involves several low-frequency phonons. In other words, it is a high-order process. At a surface numerous combinations of low-frequency modes can accept energy, rendering a short lifetime to the excited state of the stretch mode.

The calculation of the lifetime τ_i of the ith excited state is not straightforward because the relaxation mechanism is complicated. We take H/Si as an example. The lifetime of the first excited state of the H/Si(111) stretch mode has been measured experimentally[24] and the value is $\tau_1 = 0.8$ ns, whereas the theoretical value varies among different approaches. *Ab initio* molecular-dynamics simulation gave a lifetime in excess of 20 ns for the H/Si(100) system,[25] which is much longer than the experimental result. Gai and Voth,[26] using the Bloch-Redfield theory combined with classical molecular-dynamics simulations, gave $\tau_1 = 1.7 \pm 0.1$ ns for H/Si(111), which is about twice the experimental value. However, their calculation cannot determine τ_2 accurately. For H/Si(100) system, Andrianov and Saalfrank[27] gave $\tau_1 = 1.53$ ns at 300 K, which is in agreement with the experimental result of 1.2 ns.[28] They argued that the relaxation mechanism is mainly due to two-phonon process, while others attribute it to one-phonon process[29] or four-phonon process.[30,31] A simple scaling law has also been suggested for lowly excited states,

$$\tau_n = \frac{\tau_1}{n}. \tag{46}$$

However, this scaling law is not as accurate for the stretch mode as for the wagging mode and underestimates the lifetime of stretch mode excitations. The four-phonon process decays exponentially with increasing temperature.[30] However, in the one- or two-phonon process, the dependence is somehow weaker.[27,29]

V. PROBABILITY OF EXCITATION OF THE STRETCH MODE

The probability of excitation of the stretch mode can be evaluated through a set of master equations using the transition rates derived previously. Since the probability to the third or higher excited state is very small, we consider the excitations only up to the second excited state. As a result, the master equations are given by

$$\frac{dn_2}{dt} = (A_{12}+B_{12})(n_1-n_2) + (A_{02}+B_{02})(n_0-n_2) + w_{\text{pooling}}^{11\to02} n_1^2 - w_{\text{pooling}}^{02\to11} n_2 n_0 - \frac{n_2}{\tau_2}, \tag{47}$$

$$\frac{dn_1}{dt} = (A_{01}+B_{01})(n_0-n_1) + (A_{12}+B_{12})(n_2-n_1) - 2w_{\text{pooling}}^{11\to02} n_1^2 + 2w_{\text{pooling}}^{02\to11} n_2 n_0 + \frac{n_2}{\tau_2} - \frac{n_1}{\tau_1}, \tag{48}$$

$$\frac{dn_0}{dt} = (A_{01}+B_{01})(n_1-n_0) + (A_{02}+B_{02})(n_2-n_0) + w_{\text{pooling}}^{11\to02} n_1^2 - w_{\text{pooling}}^{02\to11} n_2 n_0 + \frac{n_1}{\tau_1}. \tag{49}$$

In the equations above, A_{ij} represents the transition rate from the ith state to the jth state induced by the laser and it is generally time and frequency dependent. B_{ij} represents the thermal transition rate and it can always be omitted in the following discussions since we focus on the temperature range where the thermal energy is much smaller than the excitation energy of the stretch mode. For most adatom-substrate systems, this temperature range is below hundreds of kelvins. For H/Si(111), it is below 700 K. w_{pooling} in the master equations is the transition rate of the pooling process given in Sec. IV B. τ_i is the lifetime of the ith excited state. In the equations, due to the selection rule and large off-resonance, we omit the $|0\rangle \rightarrow |2\rangle$ one-photon transition.

In the master equation above, there are two mechanisms for the adatom-substrate bond to reach the second excited state. One is direct photon absorption, which is described by either A_{01} and A_{12} or A_{02} in the master equations. The other is pooling, which is given by w_{pooling}. In the discussions below, we will consider the probability induced by each mechanism separately and compare their relative importance.

A. Probability of excitation to the first excited state

Before solving the above master equations, we first discuss the excitation probability to the first excited state. Because the probabilities of higher excited states are generally much smaller than that of the first excited state, we omit higher excitations and reduce the master equations to

$$\frac{dn_1}{dt} = A(n_0-n_1) - \frac{n_1}{\tau_1}, \tag{50}$$

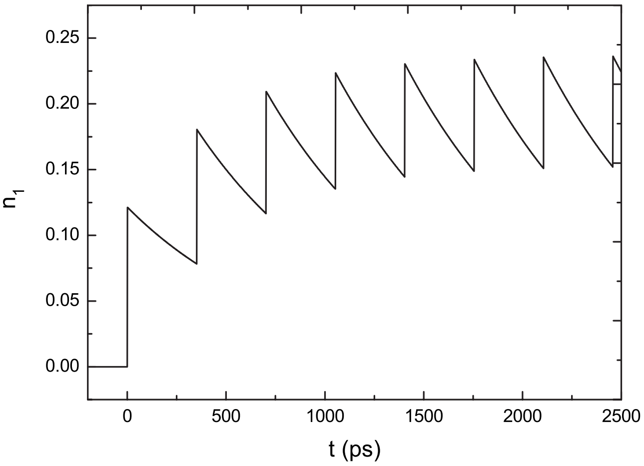

FIG. 5. The numerical results of probability in the first excited state n_1 in the case of a pulsed laser. The duration of the pulse is 1 ps and the interval between two pulses is 350 ps. The laser starts at $t=0$.

$$\frac{dn_0}{dt} = A(n_1 - n_0) + \frac{n_1}{\tau_1}, \tag{51}$$

where we have used A for A_{01}. We will discuss two cases, a continuous-wave (cw) laser and a pulsed laser.

For a cw laser, $A=w_{01}=F\sigma$ is time independent. When the system is in a steady state, the probability to the first excited state is

$$n_1 = \frac{A}{2A + 1/\tau_1}. \tag{52}$$

For a pulsed laser, when the duration t_0 of the pulse is much shorter than the interval T between two consecutive pulses, we can treat the laser as a series of δ functions,

$$A = A_0 \sum_n \delta(t - nT), \tag{53}$$

where $A_0=w_{01}t_0$ is the transition possibility in each pulse. Using $n_0+n_1=1$, Eq. (50) is rewritten as

$$\frac{dn_1}{dt} = A_0(1 - 2n_1)\sum_n \delta(t - nT) - \frac{n_1}{\tau_1}. \tag{54}$$

In the numerical calculations, we broaden the δ function to a square pulse with a duration of 1 ps. The numerical result is given in Fig. 5.

Between the pulses, $nT<t<(n+1)T$, Eq. (54) can be solved exactly, yielding

$$n_1(t) = n_1(nT + 0^+)e^{-(t-nT)/\tau_1}. \tag{55}$$

When $n\gg 1$, the system reaches a steady state and for any t we have

$$n_1(nT + t) = n_1[(n + m)T + t] \tag{56}$$

and

$$n_1(nT + 0^+) = e^{T/\tau_1} n_1(nT + 0^-). \tag{57}$$

With Eqs. (54) and (57), we get

$$n_1(nT + 0^+) = \frac{(1 - e^{-2A_0})/2}{1 - e^{(-T/\tau_1 - 2A_0)}}. \tag{58}$$

The average probability of finding an oscillator in its first excited state is given by

$$\bar{n}_1 = \frac{1}{T}\int_0^T n_1(nT + 0^+)e^{-t/\tau_1}dt = \frac{n_1\tau_1(nT + 0^+)}{T}(1 - e^{-T/\tau_1}). \tag{59}$$

In the limit $T\ll\tau_1$, $n_1(nT+0^+)\approx n_1(nT+0^-)\approx\bar{n}_1$. Using $1-e^{-T/\tau_1}\approx T/\tau_1$ and $1-e^{-2A_0}\approx 2A_0$, we get

$$n_1 = \frac{A_0/T}{2A_0/T + 1/\tau_1}. \tag{60}$$

Comparing it with Eq. (52), we get the effective transition rate $A=A_0/T=\sigma F t_0/T$. It is clear that if the lifetime of the excited state of the stretch mode is much longer than the interval of the pulse, the laser can be treated as a cw mode with an effective flux $F^*=t_0F/T$.

Next we consider the fluence dependence. We first discuss two extreme situations: $A\ll(1/\tau_1)$ and $A\gg(1/\tau_1)$. When $A\ll(1/\tau_1)$, Eq. (52) is reduced to

$$n_1 = A\tau_1 = F\sigma\tau_1, \tag{61}$$

and the dependence on flux (intensity) is linear. When $A\gg(1/\tau_1)$, we get $n_1=0.5$, which is the saturation value and is independent of the flux. We note that the number of photon absorbed is often lower than the order of the dependence on the laser flux.

B. Probability of the second excited state induced by multiphoton absorption

In this subsection, we omit the pooling and consider only the effect of direct multiphoton absorption. There are two kinds of multiphoton absorption. One is one-by-one absorption. In this process the bond first absorbs a photon to reach the first excited state and before dropping back to the ground state it absorbs another photon to jump to the second excited state. Because of the anharmonicity, at least one of the two steps must be off-resonance. It is described by A_{01} and A_{12} in the master equations. The other one is two-photon absorption, in which the adatom absorbs two photons simultaneously. It is described by A_{02} in the master equations.

We first discuss the one-by-one absorption and ignore two-photon absorption. The master equations can then be reduced to

$$\frac{dn_2}{dt} = A_{12}(n_1 - n_2) - \frac{n_2}{\tau_2}, \tag{62}$$

$$\frac{dn_1}{dt} = A_{01}(n_0 - n_1) + A_{12}(n_2 - n_1) + \frac{n_2}{\tau_2} - \frac{n_1}{\tau_1}, \tag{63}$$

$$\frac{dn_0}{dt} = A_{01}(n_1 - n_0) + \frac{n_1}{\tau_1}. \tag{64}$$

Using $n_0+n_1+n_2=1$, we obtain

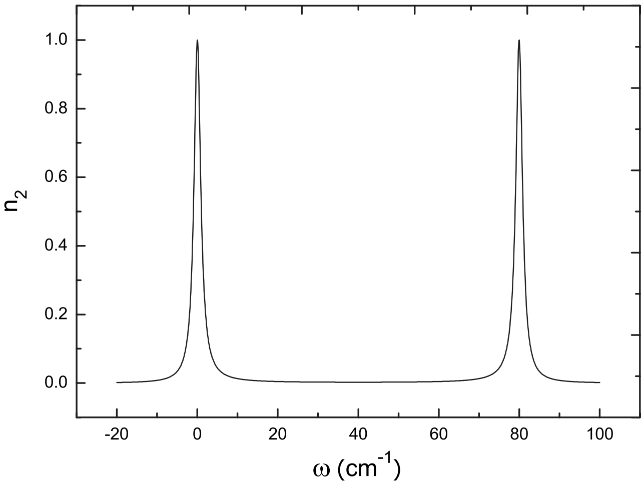

FIG. 6. The dependence of the probability in the second excited state n_2 on the monochromatic laser frequency ω. n_2 is normalized to 1. The anharmonicity here is 80 cm^{-1} and ω_{12} is set as the reference point.

$$n_2 = \frac{A_{12}A_{01}}{3A_{12}A_{01} + 2A_{01}\frac{1}{\tau_2} + A_{12}\frac{1}{\tau_1} + \frac{1}{\tau_1\tau_2}}, \tag{65}$$

$$n_1 = \frac{\left(A_{12} + \frac{1}{\tau_2}\right)A_{01}}{3A_{12}A_{01} + 2A_{01}\frac{1}{\tau_2} + A_{12}\frac{1}{\tau_1} + \frac{1}{\tau_1\tau_2}}. \tag{66}$$

Here both A_{01} and A_{12} depend on ω and t. Because of the large anharmonicity, the $|0\rangle \rightarrow |1\rangle$ and $|1\rangle \rightarrow |2\rangle$ transitions cannot be resonant simultaneously. If A_{01} is large, A_{12} is small. In this case, we get

$$n_2 \approx A_{12}\tau_2/2, \tag{67}$$

which is the saturation value. If A_{12} and A_{01} are both small (compared to $1/\tau$), we have

$$n_2(\omega) \approx A_{01}\tau_1 A_{12}\tau_2 \propto \frac{\gamma_1\gamma_2 E_0^4}{\pi^2[(\omega_{01}-\omega)^2 + \gamma_1^2][(\omega_{12}-\omega)^2 + \gamma_2^2]}. \tag{68}$$

For the frequency dependence, n_2 has two peaks at $\omega = \omega_{12}$ and $\omega = \omega_{01}$ as shown in Fig. 6.

If the laser has a finite spectral width Γ, we should replace $\frac{1}{2}\varepsilon_0 E_0^2 c$ with $\int \rho(\omega) d\omega$, where $\rho(\omega)$ is the frequency distribution of the laser. We assume that ρ is a Lorentzian with the central frequency at ω_c,

$$\rho(\omega) = \frac{\Gamma/2\pi}{(\omega - \omega_c)^2 + (\Gamma/2)^2}. \tag{69}$$

Now n_2 becomes

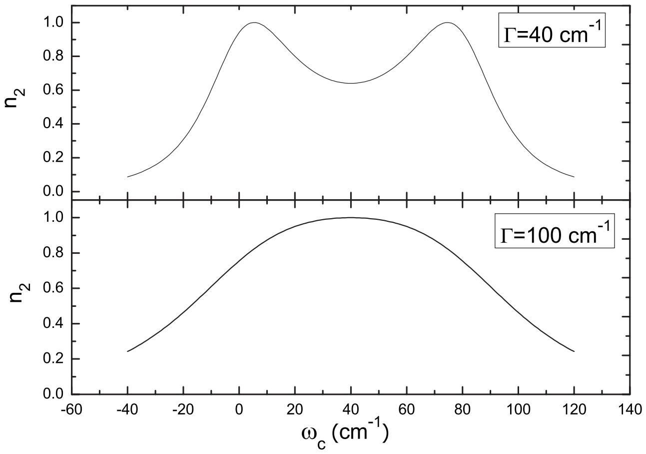

FIG. 7. The dependence of the probability in the second excited state n_2 on the central frequency ω_c of the dispersed laser. The dispersion Γ is given in the figure. n_2 is normalized to 1. The anharmonicity is 80 cm^{-1} and ω_{12} is set as the reference point.

$$n_2 \propto \int \rho(\omega) \frac{\gamma_1}{\pi[(\omega_{01}-\omega)^2 + \gamma_1^2]} d\omega \times \int \rho(\omega') \frac{\gamma_2}{\pi[(\omega_{12}-\omega')^2 + \gamma_2^2]} d\omega'. \tag{70}$$

If $\Gamma \gg \gamma_1, \gamma_2$, we get

$$n_2 \propto \frac{\Gamma/2\pi}{(\omega_{01}-\omega_c)^2 + (\Gamma/2)^2} \frac{\Gamma/2\pi}{(\omega_{12}-\omega_c)^2 + (\Gamma/2)^2}. \tag{71}$$

If the dispersion of the laser is much smaller than the anharmonicity, we have

$$n_2\left(\omega_c \approx \frac{\omega_{01}+\omega_{12}}{2}\right) \propto \frac{\Gamma^2/(2\pi)^2}{(\omega_{01}-\omega_c)^2(\omega_{12}-\omega_c)^2} \tag{72}$$

and

$$n_2(\omega_c \approx \omega_{01}, \omega_{12}) \propto \frac{1}{\pi^2(\omega_{01}-\omega_{12})^2}. \tag{73}$$

Similar to a monochromatic laser, n_2 has two peaks at $\omega_c = \omega_{01}$ and $\omega_c = \omega_{12}$ (Fig. 6).

When the dispersion of the laser increases, as shown in Fig. 7, the two peaks in Fig. 6 will move to the center (the top panel of Fig. 7). If the dispersion is large enough, even larger than the anharmonicity, the two peaks can merge into one single peak and the maximum of n_2 is at $\omega = (\omega_{01} + \omega_{12})/2$ (the bottom panel of Fig. 7).

Now we focus on two-photon absorption and ignore all other mechanisms. Since two-photon absorption is a second-order process, it is generally weak. The master equation is now given by

$$\frac{dn_2}{dt} = A_{02}(n_0 - n_2) - \frac{n_2}{\tau_2}. \tag{74}$$

We get

$$n_2 = \frac{A_{02}\tau_2}{1 + A_{02}\tau_2} n_0 \approx A_{02}\tau_2 n_0. \tag{75}$$

If the two-photon absorption is the most important mechanism of the system, the probability of the second excited state is given by the equation above. We also notice that if n_1 and n_2 are small, i.e., $n_0 \approx 1$, we have

$$n_2 \approx A_{02}\tau_2. \tag{76}$$

C. Probability of the second excited state induced by energy pooling

As mentioned already, a pooling process can occur via the off-resonant energy transfer between the adatoms: One adatom may be highly excited by acquiring multiple phonons from its neighbors. For simplicity, we focus on investigating the probability of an adatom reaching the second excited state via pooling. We assume that the laser is strong enough to pump adatoms from the ground state to the first excited state, keeping n_1 and n_0 constant. In this case, the master equation is

$$\frac{dn_2}{dt} = w_{\text{pooling}} n_1^2 - \frac{n_2}{\tau_2}. \tag{77}$$

In the above, we have omitted the reverse process, which is small since n_2 and $w_{\text{pooling}}^{02\to 11}$ are generally smaller than n_1 and $w_{\text{pooling}}^{11\to 02}$, respectively. For the steady state, namely, $dn_2/dt = 0$, we get

$$n_2 = \tau_2 w_{\text{pooling}} n_1^2. \tag{78}$$

This shows that the probability of pooling increases with n_1. Since n_1 depends on the laser, the probability of pooling depends on the laser implicitly. The pooling probability achieves maximum value only when n_1 achieves maximum value. In other words, the laser must be resonant with the $|0\rangle \to |1\rangle$ transition, i.e., $\omega = \omega_{01}$. As the dispersion of the laser increases with the laser power staying the same, photons are not absorbed by the $|0\rangle \to |1\rangle$ transition efficiently and n_1 will decrease. If the dispersion is much larger than the linewidth of one-photon absorption, we find

$$n_1 \propto \int d\omega \frac{\Gamma/2\pi}{(\omega - \omega_{01})^2 + (\Gamma/2)^2} \frac{\gamma_1/\pi}{(\omega - \omega_{01})^2 + \gamma_1^2} \approx \frac{2}{\pi\Gamma}, \tag{79}$$

where Γ and $2\gamma_1$ is the dispersion of the laser and the linewidth of one-photon absorption, respectively. Because the probability of pooling is quadratic in n_1, it is proportional to Γ^{-2}.

The excitation probability to the higher excited states can be evaluated similarly. If the lifetime of the excited state is long enough, the oscillator has the possibility to reach highly excited state through a series of pooling.

D. Comparison and discussion

So far, we have considered two main processes via which an adatom-substrate bond can reach the second excited state, i.e., pooling and multiphoton absorption. Both of the mechanisms depend on the lifetime, dipole moment, and anharmonicity of the adatom-substrate bond, which are the intrinsic properties of the system. In general, the probability of excitation increases with the lifetime and dipole moment but decreases with the anharmonicity. In addition, the probability of excitation depends on the properties of the lasers applied: its power and its frequency dispersion. Specifically, the pooling mechanism depends additionally on the strength of the dipole interaction and the coupling between the stretch mode and the substrate phonons. We now compare these two mechanisms and see how they differ in characteristics and which mechanism is more important under a given situation.

Without doing any calculation, we can point out that the two different mechanisms depend on the laser frequency very differently. On the one hand, since the dependence of n_1 on the laser frequency has a single peak at $\omega = \omega_{01}$, the pooling mechanism also has a single peak at $\omega = \omega_{01}$ according to Eq. (78). On the other hand, the multiphoton-absorption process has either two peaks if one-by-one absorption dominates or three peaks if two-photon absorption cannot be ignored.

We next consider the effect of the laser power on the excitation probability of the second excited state induced by each mechanism in the case of a cw laser. We assume that the laser is not very strong, namely, the probability of excitation is far away from saturation. For this case, we have $n_1 = w_{01}\tau_1$ according to Eq. (52). Since the probability of excitation induced by pooling is given by Eq. (78), we obtain

$$n_2^{\text{pooling}} \approx w_{\text{pooling}} w_{01}^2 \tau_2 \tau_1^2. \tag{80}$$

According to Eqs. (68) and (76), the probabilities induced by two-photon absorption (TPA) and by one-by-one (OBO) absorption are given respectively by

$$n_2^{\text{TPA}} = w_{02}\tau_2,$$

$$n_2^{\text{OBO}} = w_{01}\tau_1 w_{02}\tau_2, \tag{81}$$

where we have used the fact that $A_{ij} = w_{ij}$ in the case of a cw laser.

With the probability given above, we now discuss the effect of the laser power. For a monochromatic laser, we get

$$\frac{n_2^{\text{pooling}}}{n_2^{\text{TPA}}} \approx 0.24(\Delta\Omega)^2 \frac{1}{1 + (U/\eta)^2} \tau_1^2 \frac{|D_{01}|^2}{|D_{12}|^2} \frac{\gamma'}{\gamma_1} \tag{82}$$

and

$$\frac{n_2^{\text{pooling}}}{n_2^{\text{OBO}}} \approx 0.24(\Delta\Omega)^2 \frac{2}{1 + (U/\eta)^2} \frac{|D_{01}|^2}{|D_{12}|^2} \frac{\tau_1}{\gamma_1}, \tag{83}$$

where γ' is the linewidth of the two-photon absorption. For H/Si(111), $\Delta\Omega = 10\ \text{cm}^{-1}$, $\tau_1 = 0.8$ ns, $\eta = 52\ \text{cm}^{-1}$, and $\gamma_1 = 1\ \text{cm}^{-1}$. Both ratios above are much larger than 1. This shows that pooling is more dominant than multiphoton absorption in this case.

The situation becomes very different for a dispersed laser. As we have discussed in Sec. V C, when the laser dispersion Γ increases, the frequency dependence dose not change, but the probability of pooling decreases with the dispersion width as Γ^{-2}. Physically, it is because when $\omega_c = \omega_{01}$ and the

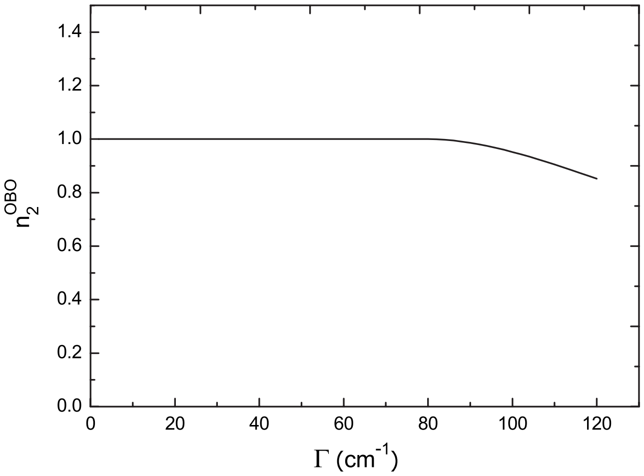

FIG. 8. The dependence of n_2^{OBO} on the dispersion Γ of the laser. The total energy is always the same and n_2^{OBO} is normalized to 1. The anharmonicity of the bond is 80 cm^{-1}.

dispersion increases, the photons cannot be absorbed resonantly, and the $|0\rangle \rightarrow |1\rangle$ transition rate decreases. However, the $|1\rangle \rightarrow |2\rangle$ transition rate increases because there are more photons that participate in the transition. We have calculated the dependence of n_2^{OBO} on Γ, which is shown in Fig. 8. It is clear that the probability induced by one-by-one photon absorption nearly stays constant as the dispersion increases. As a result, the probability of one-by-one photon absorption will become more and more important as the dispersion increases. However, when the dispersion is much larger than the anharmonicity, according to Eq. (71), the one-by-one probability will decrease as Γ^{-2}, which is the same as that of pooling. Furthermore, as the dispersion increases, the frequency dependence will change: The two satellite peaks will move to the center and finally merge into a single peak at $(\omega_{01}+\omega_{12})/2$, which is redshifted from ω_{01}.

The above analysis shows that pooling generally dominates and the multiphoton absorption can be ignored. However, as the dispersion of the laser increases, multiphoton absorption will become more important and must be taken into account.

VI. SUMMARY

In summary, we have presented a theoretical description of the excitation of an adatom-substrate bond to highly excited states, in particular, the excitation to the second excited state. There are several different mechanisms via which the bond can be highly excited, including one-by-one photon absorption, multiple photon excitation, and pooling. We have compared the excitation probabilities of these different mechanisms. We found that if the frequency dispersion of the laser is much smaller than the anharmonicity of the selected mode, the pooling process is dominant. As the frequency dispersion of the laser increases, the photon absorption (one-by-one and multiple) becomes more important. We also found that the frequency dependences of the two mechanisms are quite different: If pooling dominates, there is only a single peak in the dependence of the excitation probability on the laser frequency. If the multiphoton absorption dominates, there may exist several peaks and the main peak may exhibit a redshift. In our discussion, the H/Si(111) system has been used as an example to illustrate our analysis.

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[1] Y. J. Chabal, Surf. Sci. Rep. **8**, 211 (1988).
[2] J. W. Gadzuk and A. C. Luntz, Surf. Sci. **144**, 429 (1984).
[3] I. Hussla, H. Seki, T. J. Chuang, Z. W. Gortel, H. J. Kreuzer, and P. Piercy, Phys. Rev. B **32**, 3489 (1985).
[4] A. H. Zewail, Phys. Today **33** (11), 27 (1980).
[5] B. Wu, P. I. Cohen, L. C. Feldman, and Z. Zhang, Appl. Phys. Lett. **84**, 2175 (2004).
[6] Z. Liu, L. C. Feldman, N. H. Tolk, Z. Zhang, and P. I. Cohen, Science **312**, 1024 (2006).
[7] H.-C. Chang and G. E. Ewing, Phys. Rev. Lett. **65**, 2125 (1990).
[8] G. K. Paramonov, I. Andrianov, and P. Saalfrank, J. Phys. Chem. C **111**, 5432 (2007).
[9] R. Honke, P. Jakob, Y. J. Chabal, A. Dvorak, S. Tausendpfund, W. Stigler, P. Pavone, A. P. Mayer, and U. Schröder, Phys. Rev. B **59**, 10996 (1999).
[10] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[11] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[12] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[13] X.-P. Li and D. Vanderbilt, Phys. Rev. Lett. **69**, 2543 (1992).
[14] E. Kaxiras and J. D. Joannopoulos, Phys. Rev. B **37**, 8842 (1988).
[15] M. Nardelli, F. Finocchi, M. Palummo, R. D. Felice, C. M. Bertoni, F. Bernardini, and S. Ossicini, Surf. Sci. **269**, 879 (1992).
[16] P. Guyot-Sionnest, Phys. Rev. Lett. **67**, 2323 (1991).
[17] B. N. J. Persson, Phys. Rev. B **46**, 12701 (1992).
[18] B. N. J. Persson and R. Ryberg, Phys. Rev. B **24**, 6954 (1981).
[19] H. Lin, L.-F. Yuan, and Q.-S. Zhu, Chem. Phys. Lett. **308**, 137 (1999).
[20] P. Dumas, Y. J. Chabal, and G. S. Higashi, Phys. Rev. Lett. **65**, 1124 (1990).
[21] M. Göpper-Mayer, Ann. Phys. **401**, 273 (1931).
[22] P. Guyot-Sionnest, Phys. Rev. Lett. **66**, 1489 (1991).
[23] S. A. Corcelli and J. C. Tully, J. Chem. Phys. **116**, 8079 (2002).

[24] P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, and G. S. Higashi, Phys. Rev. Lett. **64**, 2156 (1990).
[25] J. C. Tully, Y. J. Chabal, K. Raghavachari, J. M. Bowman, and R. R. Lucchese, Phys. Rev. B **31**, 1184 (1985).
[26] H. Gai and G. A. Voth, J. Chem. Phys. **99**, 740 (1993).
[27] I. Andrianov and P. Saalfrank, J. Chem. Phys. **124**, 034710 (2006).
[28] P. Guyot-Sionnest, P. Lin, and E. Miller, J. Chem. Phys. **102**, 4269 (1995).
[29] I. Andrianov and P. Saalfrank, Chem. Phys. Lett. **350**, 191 (2001).
[30] E. T. Foley, A. F. Kam, J. W. Lyding, and P. Avouris, Phys. Rev. Lett. **80**, 1336 (1998).
[31] B. Persson and P. Avouris, Surf. Sci. **390**, 45 (1997).