Effect of temperature on the infrared and sum-frequency generation spectra of adsorbates

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The dephasing and energy relaxation contributions to the line width in infrared (IR) and sum-frequency generation (SFG) spectra of adsorbates are derived from the generalized master equation approach. Expression for the line shift is also obtained. The anharmonic interaction between the adsorbate and the substrate is expanded in a polynomial in terms of the adsorbate and phonon coordinates, and the dephasing is shown to be mainly due to two-phonon processes, while two-phonon, three-phonon or four-phonon processes can contribute to energy relaxation, depending on the relative values of the adsorbate vibrational and the phonon frequencies. The temperature-dependence data of the IR absorption for C(111):H is found to be consistent with the theory, and the large line width for C(111):D can be accounted for by the efficient two-phonon energy relaxation process which is not available for C(111):H due to the higher adsorbate vibrational frequency for C(111):H. © 1997 American Institute of Physics.

I. INTRODUCTION

Because of the important role hydrogen plays in producing high-quality diamond film in the chemical vapor deposition (CVD) process,1,2 the study of the vibrational relaxation dynamics of hydrogen adsorbed on diamond surfaces has been a subject of interest recently.3–7 Several experimental techniques have been used to probe the surface vibrational dynamics. High-resolution electron energy loss spectroscopy (HREELS) is a surface sensitive and has a wide energy range. It has been applied to the systems C(111):H and C(100):H, revealing broad bands around 2840 cm−1 and 2927 cm−1, respectively.5 However the low resolution (100 cm−1) makes the interpretation of the spectra difficult.

Infrared-visible sum-frequency generation (SFG) is a highly surface-sensitive and high resolution spectroscopic technique, and measuring the polarization dependence of the spectrum allows one to determine the orientation of the adsorbate. Applying SFG to the C(111):H system, a single CH stretch peak at 2838 cm−1 and a single CH bending peak at 1331 cm−1 were observed, and together with information from the beam polarization dependence, it was determined that the hydrogen atoms were adsorbed on-top with the CH bond along the surface normal.3 The temperature dependence of the line width and the frequency shifts of the CH stretch and bend modes have also been measured: from 300 K to 700 K, the peak frequencies shift from 2837 to 2833 cm−1 and from 1330 to 1324 cm−1, respectively, for the stretch and the bend modes, while the half-widths change from 7 to 9 cm−1, and from 5 to 7 cm−1, respectively, for these two modes. By incorporating a third picosecond infrared laser, time-resolved SFG measurements of the CH stretching vibrations have been carried out,4 yielding a value of 19 ps for the lifetime of the v = 1 state. Thus, SFG is perhaps the most versatile technique for studying surface vibrations.

In spite of its low surface sensitivity, Fourier transform infrared (FTIR) spectroscopy has been successfully employed to study the vibrational spectra of hydrogen and deuterium on C(111).6 The CH stretching peak at 2835.5 cm−1 with the temperature-independent bandwidth of 4.5 cm−1 between 100 K and 300 K, and the CD stretch at 2110 cm−1 with dramatic band broadening of 30 cm−1 had been observed, in essential agreement with HREELS and SFG measurements. Recently, a careful measurement of the line widths and shifts of the CH stretch for C(111):H in the temperature range 100-1000 K has been carried out using FTIR spectroscopy.7 Such data can provide much information about the adsorbate vibrational dynamics. The half-width at half maximum, when there exists only homogeneous broadening, can be expressed as

$$\frac{1}{T_2} = \frac{1}{T_{2*}} + \frac{1}{2T_1},$$

where $T_2*$ is the pure dephasing time, and $T_1$ is the relaxation time due to inelastic transitions. In analysing the temperature dependence of their data, J.C. Lin et al.7 employed the exchange model8–10 for both the frequency shift and the pure dephasing contribution to the width, plus a multiphonon relaxation description11,12 of the $T_1$ contribution to the width. The exchange model assumes that the high-frequency adsorbate vibration couples anharmonically to a low-frequency exchange mode which is modulated by interaction with the adsorbate–substrate vibration.

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substrate phonons, while the multiphonon description assumes weak anharmonic coupling of the adsorbate to the lattice.

While the exchange model and multiphonon relaxation provided a reasonable description of the results of Ref. 7, it is felt that it may not be necessary to postulate the existence of an exchange mode to describe the dephasing process. Thus in this paper, we shall present a theoretical treatment of the vibrational spectral line widths and shifts which is suitable for a system with high-frequency phonon distributions. Both the dephasing ($T_2^\alpha$) and energy relaxation ($T_1$) processes can be treated on the same footing. The temperature dependent data of Ref. 7 for CH stretch on diamonds will be analysed with this model.

II. GENERAL THEORY

It is well-known that the IR absorption spectrum is proportional to the imaginary part of the linear susceptibility $\chi_{ij}(\omega)$ of the system.\(^{13,14}\) $\chi_{ij}$ is related to the polarization $P_i$ induced by the electric field $E_j(\omega)$ of the IR laser of frequency $\omega$ by

$$ P_i(\omega) = \sum_j \chi_{ij}(\omega)E_j(\omega), \tag{2} $$

where $i,j$ denote the Cartesian components. $P_i$ can be computed from the density matrix of the system. In the Markovian approximation, the linear susceptibility is given by\(^{14}\)

$$ \chi_{ij}(\omega) = \frac{2i}{\hbar} \sum_{nm} \sum_T p_n \frac{\langle gn|M_j|gm\rangle \langle gm|M_i|gn\rangle}{i(\omega_{mn} - \omega) + \Gamma_{mn}}, \tag{3} $$

where $m,n$ denote the vibrational levels in the ground electronic state $g$, $\omega_{mn}$ is the transition frequency, and $p_n$ represents the Boltzmann factor (population) of the vibronic state $|gn\rangle$. $M_i$ is the $i$-th Cartesian component of the dipole moment operator of the absorbing medium, and $\Gamma_{mn}$ is the matrix element of the damping operator (see Sec. III). For IR absorption, the contribution from excited electronic states can be neglected. Under the Born–Oppenheimer (BO) approximation, the dipole moment element becomes $\langle gn|M_j|gm\rangle = \langle m|\mu_i(Q)|n\rangle$, where $\mu_i = \langle g|M_i|g\rangle$ is the dipole moment operator in the ground electronic state and is a function of the normal vibrational coordinate $Q_i$ of the system. Making a power series expansion of $\mu(Q)$ to first order in $\{Q\}$ yields

$$ \chi_{ij}(\omega) = \frac{2i \hbar}{\sum_{nm} \sum_T p_n \langle gn|\mu_i|gm\rangle \langle gm|\mu_j|gn\rangle}{i(\omega_{mn} - \omega) + \Gamma_{mn}}. \tag{4} $$

In the single band case where only one pair of vibrational levels $(m,n)$ participates in the absorption process, the absorption spectrum is proportional to

$$ \text{Im} \chi_{ij}(\omega) = \frac{2}{\hbar} \sum_T p_n \langle \frac{\partial \mu_i}{\partial Q_i} 0 \langle \frac{\partial \mu_j}{\partial Q_j} 0 |n\rangle |m\rangle^2}{(\omega_{mn} - \omega)^2 + \gamma_{mn}^2}, \tag{5} $$

which is a Lorentzian lineshape. Here, $\gamma_{mn}$ and $\delta_{mn}$ are the real and imaginary part of $\Gamma_{mn}$, respectively.

In the sum-frequency generation studies of adsorbate vibrations, an IR and a visible laser, of frequencies $\omega_1$ and $\omega_2$, respectively, are focused on the system, and the SFG signals at frequency $\omega_1 + \omega_2$ are detected. The SFG spectrum is proportional to the square of the magnitude of the second-order susceptibility $\chi_{ijk}^{(2)}$. It has been shown in Ref. 15 that under the BO approximation, the nonlinear susceptibility tensor for IR-visible SFG is given by

$$ \chi_{ijk}^{(2)}(\omega) = \frac{2i}{\hbar} \sum_{mn} \sum_T p_n \frac{\langle gn|M_i|gm\rangle \langle gm|M_j|gn\rangle \langle gn|M_k|gm\rangle}{i(\omega_{mn} - \omega) + \Gamma_{mn}}, \tag{6} $$

where $\alpha_{kj}$ is the conventional optical polarizability tensor of the system, and the Placzek approximation has also been employed. Eq. (6) shows that the system must be both IR and Raman active in order to generate a SFG signal. It follows immediately from Eq. (6) that in the single band case, the SFG signal which is proportional to $|\chi_{ijk}^{(2)}(\omega)|^2$, is a Lorentzian centered at $\omega_{mn}$ and is identical to the IR lineshape within a normalization constant. In general, a non-resonant contribution $\chi_{NR}$ should be added to Eq. (6).\(^{3,4}\) In any event, both the IR and the SFG spectra yield information about the matrix elements of the damping operator $\Gamma$, which are governed by the relaxation dynamics of the system.

III. $T_1$ AND $T_2$ RELAXATION PROCESSES

The linear susceptibility of the adsorbate can be conveniently calculated from a knowledge of the reduced density matrix $\hat{\sigma}$ of the adsorbate motion. Generally, the Hamiltonian of the total system can be written as

$$ \hat{H} = \hat{H}_s + \hat{H}_b + \hat{V}, \tag{7} $$

where $\hat{H}_s$ and $\hat{H}_b$ represent the Hamiltonians for the adsorbate vibration (the system) and the substrate phonons (the heat bath), respectively, and $\hat{V}$ denotes the interaction between the system and the heat bath. The equation of motion for $\hat{\sigma}$, known as the generalized master equation, can be conveniently derived from Zwanzig’s projection operator technique.\(^{15,14,20}\) Usually the bath has very short correlation time (the Markovian limit), in which case the reduced density matrix obeys

$$ \frac{d\hat{\sigma}}{dt} = -i\hat{L}_s + i\hat{L}_\text{ext} + \hat{\Gamma} \hat{\sigma}, \tag{8} $$

where $\hat{L}_s = (1/\hbar)[\hat{H}_s, \hat{\sigma}]$ is the Liouville operator for the system, $\hat{L}_\text{ext} = (1/\hbar)[\hat{H}_\text{ext}, \hat{\sigma}]$ with $\hat{H}_\text{ext} = -\mu \cdot \hat{E}(t)$ representing the interaction with the external electromagnetic field $\hat{E}(t)$, and $\hat{\Gamma}$ is damping operator whose matrix elements are related to the Zwanzig tetradic evaluated at the appropriate eigenfrequencies of $\hat{L}_s$.\(^{14,20,21}\)

Because of the anharmonicity of the CH bond in C(111):H, the $1 \rightarrow 2$ transition is 110 cm$^{-1}$ lower than the
0→1 fundamental, and hence each n→m transition can be considered to be an isolated line. In this case the macroscopic polarization of the system is given by

$$\tilde{P}(t) = \text{Tr}_s \tilde{\mu}(t) = \tilde{\mu}_m \sigma_{mn} + \text{c.c.},$$  \hspace{1cm} (9)

where $\tilde{\mu}$ is the dipole moment operator for the adsorbate, $\text{Tr}_s$ denotes a trace over the system variables, and c.c. represents the complex conjugate. Hence the spectrum is determined by the off-diagonal reduced density matrix element $\sigma_{mn}$. For the case of an isolated line, the equation of motion of $\sigma_{mn}$ is

$$\frac{d\sigma_{mn}}{dt} = -i \omega_{mn} \sigma_{mn} - \frac{i}{\hbar} (\sigma_{mn} - \sigma_{nm}) (H_{\text{ext}})_{mn},$$  \hspace{1cm} (10)

where

$$\omega_{mn} = \omega_{mn}^0 + \Delta \omega_{mn}^{(1)},$$  \hspace{1cm} (11)

with $\omega_{mn}^0 = (1/\hbar) (E_m - E_n)$ being the unperturbed frequency and $\Delta \omega_{mn}^{(1)}$ the first-order spectral shift

$$\Delta \omega_{mn}^{(1)} = \frac{1}{\hbar} \sum \rho^{(b)}_{aa} (V_{m,a,m} - V_{n,a,n}).$$  \hspace{1cm} (12)

Solving Eq. (10) in the linear response regime\(^{(4)}\) shows that in the Markovian limit, the spectrum is a Lorenzian with a width:

$$\gamma_{mn} = \text{Re} \Gamma_{mn}^{\text{in}} = \frac{1}{2} \left( \frac{1}{T_{1m}} + \frac{1}{T_{1n}} \right) + \gamma_{mn}^{(d)},$$  \hspace{1cm} (13)

where the inelastic contributions are

$$\frac{1}{T_{1k}} = \frac{2 \pi}{\hbar^2} \sum_{\alpha, \beta} \sum_{m, m'} \rho^{(b)}_{\alpha \beta} \left| V_{k,a,m,m'} \right|^2 \delta (\omega_{k,a,m' \beta}), \hspace{1cm} k = m, n,$$

and the elastic or dephasing contribution is

$$\frac{1}{T_2} = \gamma_{mn}^{(d)} = \frac{\pi}{\hbar^2} \sum_{\alpha, \beta} \rho^{(b)}_{\alpha \beta} \left| V_{m,a,m, \beta} - V_{n,a,n, \beta} \right|^2 \delta (\omega_{\alpha \beta}).$$  \hspace{1cm} (14)

Similarly the second order shift is given by

$$\Delta \omega_{mn}^{(2)} = \text{Im} \Gamma_{mn}^{\text{in}} = \frac{1}{\hbar^2} \rho \sum_{\alpha, \beta} \sum_{m, m'} \frac{\left| V_{m,a,m' \beta} \right|^2}{\omega_{m,a,m' \beta}} - \frac{\left| V_{n,a,m' \beta} \right|^2}{\omega_{n,a,m' \beta}},$$  \hspace{1cm} (16)

where $P$ denotes the principal value. In the above formulae, $m, \alpha$ denote the eigenstates of $\hat{H}_s, \hat{H}_b$ with energy eigenvalues $E_m, E_\alpha$, respectively, $\hbar \omega_{\alpha \beta} = E_\alpha - E_\beta$, and $\hbar \omega_{m,a,m' \beta} = E_m - E_n + E_\alpha - E_\beta \cdot 1/T_{1n}$ and $1/T_{1n}$ represent the rates of inelastic transitions out of the levels $m$ and $n$, respectively, and are identical to the results obtained from Fermi’s golden rule.

**IV. MODEL FOR VIBRON-PHONON COUPLINGS**

To treat the temperature effect on the spectral width and shift, we shall consider the following model of a single adsorbate vibrational mode $Q$ (the vibron) representing the CH or CD stretch, interacting with the phonon modes $\{q_i\}$. Thus $\hat{H}_s$ and $\hat{H}_b$ are given by

$$\hat{H}_s = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} \Omega^2 Q^2,$$

$$\hat{H}_b = \sum_i \left( -\frac{\hbar^2}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \omega_i^2 q_i^2 \right),$$

and the anharmonic interaction potential between the vibron and the phonons are expanded as

$$\hat{V} = \hat{V}_c + \hat{V}_q + \cdots$$

in which the cubic and quartic interactions are

$$\hat{V}_c = \frac{1}{3!} \sum_i b_i q_i Q^2 + \sum_{i,j} b_{ij} q_i q_j Q,$$

and

$$\hat{V}_q = \frac{1}{4!} \sum_i c_i q_i Q^3 + \sum_{i,j} c_{ij} q_i q_j Q^2$$

$$+ \sum_{i,j,k} c_{ijk} q_i q_j q_k Q.$$  \hspace{1cm} (21)

Here, $\Omega$ is the harmonic frequency of the adsorbate mode undergoing spectral transition, $\omega_i$ is the phonon frequency of the $i$-th mode, and the coefficients in the cubic and quartic interactions are given by the following partial derivatives of the interaction potential evaluated at the equilibrium configuration: $b_i = [\delta^3 \hat{V} / \delta q_i \delta q_i \delta Q^2]_0$, $b_{ij} = [\delta^3 \hat{V} / \delta q_i \delta q_j \delta Q]_0$, $c_i = [\delta^4 \hat{V} / \delta q_i \delta q_i \delta q_i Q]_0$, $c_{ij} = [\delta^4 \hat{V} / \delta q_i \delta q_j \delta q_i Q]_0$, and $c_{ijk} = [\delta^4 \hat{V} / \delta q_i \delta q_j \delta q_k \delta Q]_0$.

To calculate the contribution of various anharmonic terms to the spectral width and shift, we first express $Q$ and $q_i$ in terms of the vibron and phonon creation and annihilation operators as

$$Q = \sqrt{\frac{\hbar}{2\Omega}} (b + b^\dagger), \hspace{1cm} q_i = \sqrt{\frac{\hbar}{2\omega_i}} (b_i + b_i^\dagger).$$  \hspace{1cm} (22)

The unperturbed Hamiltonians then take the simple forms

$$\hat{H}_s = \hbar \Omega \left( b^\dagger b + \frac{1}{2} \right), \hspace{1cm} \hat{H}_b = \sum_i \hbar \omega_i \left( b_i^\dagger b_i + \frac{1}{2} \right).$$  \hspace{1cm} (23)

The unperturbed eigenstate of the system is specified by its vibrational quantum number $m$ with energy $E_m = (m + \frac{1}{2}) \hbar \Omega$, while the state of the bath is specified by the occupation numbers of each phonon mode $\alpha = \{n_i\}$ so that $E_{\alpha} = \Sigma_i (n_i + \frac{1}{2}) \hbar \omega_i$. Substituting the interaction potential of Eqs. (19)–(21) into Eq. (12) gives the first order shift. Since only the diag...
only the cubic and quartic interactions can contribute to the shift. The general result is very tedious and will not be presented here. We will give the dominant contribution to the $\Delta \omega_{mn}^{(2)}$ under the quasi-mode approximation in the next section.

V. THE QUASI-MODE APPROXIMATION

The anharmonic interaction $\hat{V}$ is of short range since the adatom will interact strongly only with the substrate atoms near it. For simplicity, we shall follow Persson and coworkers$^{10-12}$ and assume that $\hat{V}$ depends only on the relative normal displacement between the adatom of mass $m_a$ and the surface atom of mass $m_s$ directly below it:

$$\hat{V} = U(u_a - u_s),$$

where we have used the relation $\tilde{n}_l^+ = \tilde{n}_l \exp(h\omega_l/kT)$ and the property of the delta function to factor out the Boltzmann factor $\exp(-h\Omega/kT)$. The spectral density function $q'(\omega, \omega')$ is defined by

$$q'(\omega, \omega') = \sum_{i,j} \tilde{b}_{ij} \delta(\omega - \omega_i) \delta(\omega' - \omega_j).$$

Note that $b_{ij} \sim O(1/N)$ (see next section) and hence the $i = j$ terms make negligible contributions in the continuum limit. In Eq. (31) we have considered both the excitation ($m' = m + 1$) and the de-excitation ($m' = m - 1$) inelastic processes. Only the de-excitation processes have been included in Refs. 7, 11, 12 and the above-mentioned Boltzmann factor is absent in their analysis, which could be important if the vibron frequency $\Omega$ is not too large.

Similarly, only the terms $c_{ijk} q_i q_j Q$ in the quartic interaction will contribute to the $T_1$-process, yielding

$$\left( \frac{1}{T_{1|m/q}} \right) = \frac{2 \pi \hbar^2}{16(4!)^2 \Omega} \sum_{i,j,k} \frac{c_{ijk}^2}{\omega_i \omega_j \omega_k} \times (\tilde{n}_i + 1)(\tilde{n}_j + 1)(\tilde{n}_k + 1) \delta(\Omega - \omega_i - \omega_j - \omega_k)$$

$$\times g(\omega, \omega', \Omega - \omega - \omega') \left[ \tilde{n}(\omega) + 1 \right] \left[ \tilde{n}(\Omega - \omega - \omega') + 1 \right],$$

where

$$g(\omega, \omega', \omega'') = \sum_{i,j,k} \tilde{c}_{ijk} \delta(\omega - \omega_i) \delta(\omega' - \omega_j) \delta(\omega'' - \omega_k).$$

The second order shift $\Delta \omega_{mn}^{(2)}$ can similarly be evaluated. Without the restriction of the delta functions appearing in the expressions for the width, all the terms in $\tilde{V}_c$ and $\tilde{V}_q$ will contribute to the shift. The general result is very tedious and will not be presented here. We will give the dominant contribution to $\Delta \omega_{mn}^{(2)}$ under the quasi-mode approximation in the next section.
\[ u_z = \sum_i \frac{1}{\sqrt{Nm_i}} P(\omega_i)(\hat{e}_i, \hat{z}) q_i, \]

(36)

where \( N \) is the number of phonon modes, \( \hat{e}_i \) is the polarization vector of the phonons of mode \( i \), and \( \hat{z} \) is the unit vector normal to the surface. \( P(\omega_i) \) is the reduction factor which in the \( m_i \ll m \) limit has been shown\(^{10} \) to be \( P(\omega_i) = -\frac{\omega_i^2}{(\omega_i^2 - \Omega^2)^2} \). The effect of the reduction factor is less dramatic for the C(111):H system than the CO/Pt system studied by Persson and Rydberg\(^{10} \) since in the former system, \( \Omega \approx 2835 \text{ cm}^{-1} \) and \( \omega_i \approx 1200 \text{ cm}^{-1} \), while for the latter, \( \Omega \approx 460 \text{ cm}^{-1} \) and \( \omega_i \approx 70 \text{ cm}^{-1} \). More general model can also be employed\(^{16} \) where it was pointed out that the reduction effect is absent for modes vibrating parallel to the surface and \( P(\omega_i) \) becomes unity.

Making a Taylor series expansion of \( U \) about the equilibrium separation, the coefficients of \( \hat{V}_r \) and \( \hat{V}_q \) that contribute to the line width and line shift can be expressed in terms of the derivatives of \( U \) at equilibrium, \( U_0^{(n)} = [d^n U(r)/dr^n]_{\text{eq}} \), as

\[ b_{ij} = \frac{1}{N} BP(\omega_i) P(\omega_j)(\hat{e}_i, \hat{z})(\hat{e}_j, \hat{z}), \]

\[ c_{ij} = \frac{1}{N} CP(\omega_i) P(\omega_j)(\hat{e}_i, \hat{z})(\hat{e}_j, \hat{z}), \]

\[ c_{ijk} = \frac{1}{N^2} C' P(\omega_i) P(\omega_j) P(\omega_k)(\hat{e}_i, \hat{z})(\hat{e}_j, \hat{z})(\hat{e}_k, \hat{z}), \]

where \( B = 3U_0^{(1)}/(m \sqrt{m_i}), \ C = 6U_0^{(2)}/(mm_i), \ C' = (2/3)(\sqrt{m_i}/m)C \). It follows that the density functions \( p(\omega), q(\omega, \omega'), q'(\omega, \omega'), \) and \( g(\omega, \omega', \omega'') \) can be expressed in terms of the projected phonon density of states\(^{10} \)

\[ \rho_c(\omega) = (1/N) \sum_i (\hat{e}_i, \hat{z})^2 \delta(\omega - \omega_i). \]

(38)

Hence both the line width and the line shift depend on \( \rho_c(\omega) \), which in principle can be obtained from first-principles calculations\(^{17,18} \). Often there exist a large and sharp peak at \( \omega = \bar{\omega} \) in the phonon density of state, and as a first approximation, we replace \( \rho_c(\omega) \) by a Lorentzian with a small half-width \( \gamma_0 \):

\[ \rho_c(\omega) = \frac{\gamma_0}{\pi(\omega - \bar{\omega})^2 + \gamma_0^2}, \]

(39)

In this \textit{quasi-mode approximation} (QA), we assume that in the integrands in Eqs. (27), (29), (31), and (33), the factors multiplying \( \rho_c \) are slowly varying functions of \( \omega \) so that they can be evaluated at the quasi-mode frequency \( \bar{\omega} \) and factored outside the integrals. The remaining integrals can readily be evaluated, yielding the following QA results:

\[ \Delta \omega_{mn}^{(1)} = \delta \omega_0(\bar{n}(\bar{\omega}) + \frac{1}{2}), \]

(40)

\[ \gamma_{mn}^{(d)} = \frac{\delta \omega_0^2}{4\gamma_0} n(\bar{\omega}) \bar{n}(\bar{\omega} + 1), \]

(41)

\[ \frac{1}{T_{1m_c}} = A_c [m + (m + 1)e^{-\hbar \Omega/kT}] \frac{n(\bar{n}(\omega) + 1)}{\bar{n}(\bar{\omega}) + 1}, \]

(42)

\[ \frac{1}{T_{1m_q}} = A_q [m + (m + 1)e^{-\hbar \Omega/kT}] \frac{n(\bar{n}(\omega) + 1)^2}{\bar{n}(\bar{\omega} + 1)} \frac{n(\bar{n}(\omega) + 1)}{\bar{n}(\bar{\omega}) + 1}, \]

(43)

where

\[ A_c = \frac{\pi \hbar B^2 P(\omega)^2 P(\Omega - \bar{\omega})^2}{4(3!)^2 \Omega \omega(\Omega - \bar{\omega})} \rho_c(\Omega - \bar{\omega}), \]

\[ A_q = \frac{\pi \hbar^2 C^2 P(\omega)^4 P(\Omega - 2\bar{\omega})^2}{8(4!)^2 \Omega^2 \omega^2 (\Omega - 2\bar{\omega})} \rho_c(\Omega - 2\bar{\omega}), \]

and

\[ \delta \omega = \frac{\hbar C(m-n)P(\omega)^2}{4! \Omega \bar{\omega}}. \]

Relations similar to Eqs. (40) and (41) for the first order shift and the dephasing rate have been derived in Ref. 10 using a different method.

Finally we consider the second order shift. The general expression is given by Eq. (16), and as mentioned at the end of last section, many terms contribute to this shift. However, the dominant contribution will come from terms for which the frequency denominators in Eq. (16) are small, and for the hydrogen/diamond system, in the QA limit, these correspond to \( |\omega_{\text{ma,ma}}| = |\Omega - 2\bar{\omega}| \), coming from \( b_{ij}, q, \Omega \) term in \( \hat{V}_q \).

Thus,

\[ \Delta \omega_{mn}^{(2)} = \nu [n(\bar{n}(\omega) + \frac{1}{2})], \]

(44)

where

\[ \nu = \frac{2(m-n)B^2 P(\omega)^2}{\hbar^2 (3!)^2 (\Omega - 2\bar{\omega})}. \]

Eq. (44) has the same dependence on \( n(\bar{n}(\omega)) \) as the first order shift \( \Delta \omega_{mn}^{(1)} \). Other second-order contributions can have higher order dependence on \( n(\bar{n}(\omega)) \).

VI. DISCUSSIONS

We shall first apply the results of the previous sections to the fundamental bands \((m=1 \text{ and } n=0)\) of C(111):H and C(111):D. For C(111):H, the adsorbate vibrational frequency is \( \Omega = 2835 \text{ cm}^{-1} \), while the phonon frequencies are below 1400 cm\(^{-1} \). Thus a two-phonon process cannot satisfy the energy conservation requirement of Eq. (31), and \( (1/T_{1c})_c = 0 \). Combining Eqs. (13), (41), and (43), the line width is given by

\[ \gamma_{10} = \frac{\delta \omega_0}{4\gamma_0} n(\bar{n}(\omega)) \left[ n(\bar{n}(\omega) + 1) + \frac{1}{2} A_c [1 + 2e^{-\hbar \Omega/kT}] \right] \]

\[ \times \left[ n(\bar{n}(\omega) + 1) + 1 \right] \left[ n(\bar{n}(\omega) + 1) + 1 \right], \]

(45)
where $\tilde{\omega}_1$ is the phonon mode for dephasing and $\tilde{\omega}_2$ is the high-frequency phonon mode responsible for relaxation. From Eqs. (40) and (44), we obtain for the line shift

$$\Delta \omega_{10} = (\Delta \omega + \nu)(\tilde{\omega}_1 + \frac{\tilde{\omega}_2}{2}).$$

According to Eqs. (40) and (41), both the first-order line shift and the pure dephasing rate are related to the fourth-order derivative of the anharmonic interaction potential, $c_{ij}$. The three-phonon energy relaxation rate and the fit curve of the line width $\Delta \gamma$ are, on the other hand, determined by the other fourth-order derivative, $c_{ijk}$. As derived in Eq. (37), if the interaction potential only depends upon the internuclear separation between the adsorbed H and the adjacent C, the same fourth-order anharmonicity is responsible for both pure dephasing and energy relaxation. Thus the coupling phonon modes for both processes would be the same. If, on the other hand, the interaction potential also depends on other surrounding carbon atoms, the two fourth-order anharmonicities are not expected to be related. The coupling phonons for both cases are, therefore, not required to be the same. Here we do not impose this requirement for fitting.

In Figs. 1(a) and 1(b), we show a refitting of the temperature dependence data of J.-C. Lin et al.\textsuperscript{7} using Eqs. (45) and (46). In addition, Fig. 1(c) shows the difference between the experimental data and the fit curve of the line shift $\Delta \gamma$. From our fit of the line shift, we obtain $\tilde{\omega}_1 = 1200$ cm$^{-1}$ and $\Delta \omega = -23$ cm$^{-1}$. The accuracy of the data, unfortunately, does not allow us to determine an unambiguous value for the second order shift parameter $\nu$, which we estimate to have a magnitude smaller than 2 cm$^{-1}$. Assuming that the bending mode at 1330 cm$^{-1}$, Ref. 3, is responsible for the two high frequency surface modes as in the case of Si(111):H,\textsuperscript{23} we obtain the line width parameter of the phonon mode for dephasing, $\gamma_0$. The fit parameters of C(111):H and the extracted temperature-independent factor, $A_p$, are listed in Table I. The expressions employed here are similar to those of the exchange model used previously, except for the additional Boltzmann factor to take into account the excitation mechanism in the $T_1$ relaxation process. Since the energy of one quantum of CH vibration is several times larger than the thermal energy $kT$ even for the highest temperature used in the experiment, including this factor changes the fitting only by about 1.5%. For adsorbate systems with lower vibrational frequencies, however, this factor will be more important.

We note from Eq. (45) that the temperature dependence of the width is predominantly governed by the phonons of the lowest frequency involved in the energy exchange process. Thus for C(111):H, the width increases with temperature approximately as $[\tilde{\omega}_1(\Omega - 2\tilde{\omega}_2) + 1]$, in which $\Omega - 2\tilde{\omega}_2 = 175$ cm$^{-1}$.

For the C(111):D system, the CD stretch frequency is 2115 cm$^{-1}$,\textsuperscript{13} and two-phonon inelastic process is possible. Thus both $(1/T_{1m})_c$ and $(1/T_{1m})_d$ contribute to the line width, and it is expected that $(1/T_{1m})_c$ makes the dominant contribution in comparison with $(1/T_{1m})_d$ and $\gamma^{el}$, since in general $b_{ij}^2 > c_{ij}$. This fact has been used to explain the more efficient relaxation mechanism (larger line width) in C(111):D.\textsuperscript{27} While no temperature dependence data has been obtained for this system, it will be less pronounced compared with the C(111):H case, since the temperature dependence is now governed mainly by the factor $[\tilde{\omega}_1(\Omega_{CD} - \tilde{\omega}_2) + 1]$, with $\Omega_{CD} - \tilde{\omega}_2 = 785$ cm$^{-1}$, assuming the same value of $\tilde{\omega}_2$ as in the C(111):H case. The extracted temperature-independent factor $A_p$ is also shown in Table I.

It is instructive to compare the present system with the case of hydrogen on silicon. For the system of Si(111)-1 X 1:H, the Si-H stretch frequency is 2083.7 cm$^{-1}$.\textsuperscript{22} From time-resolved experiments, $T_1$ was found to vary from 1.4 to 0.55 ns in the temperature range of 100-450 K.\textsuperscript{22} Such long relaxation time can be explained by the fact that unlike dia-

![FIG. 1. Fitting of temperature dependence data of C(111):H. (a) and (b) show the spectral shift $\omega_{10}$ and the line width $2 \gamma_{10}$, respectively; (c) depicts the difference between the experimental data of the line width and the fitting curve as a function of the substrate temperature.](Image)
mond which has high frequency phonons, the maximum phonon frequency of the Si(111):H system is below 700 cm\(^{-1}\), and energy relaxation requires a four-phonon process. It is then necessary to include the pentatic term \(\sum d_{ijkl}q_{i}q_{j}q_{k}Q\) in the expansion of the anharmonic interaction of Eq. (19). Under the quasi-mode approximation, similar to Eqs. (42) and (43), \(T_{1m}\) is given by

\[
\left(\frac{1}{T_{1m}}\right)_{p} = A_{p}[m+(m+1)e^{-\beta E_{D}}][\eta(\omega_{p})+1]^{3}
\]

where \(A_{p}\) is proportional to \(d_{p}^{2}\) and is independent of temperature. It was found that the temperature dependence of \(T_{1}\) can be fitted very well by choosing \(\omega_{p} = 635\) cm\(^{-1}\). The dephasing time has been measured to be between >200 ps to <3 ps in the temperature range 40-500 K. As in the case of C(111):H, dephasing can proceed via the quartic interaction \(c_{ijkl}q_{i}q_{j}Q^{2}\), which in general is larger then the pentatic terms responsible for energy relaxation in Si(111):H. Under the QA, the inverse of the dephasing time is again given by Eq. (41). However, in order to fit the temperature dependence data, a value of \(\omega_{p} = 210\) cm\(^{-1}\) was obtained.

The isotope effect observed for the diamond substrate has also been observed in Si(100), where it was found that for the symmetric stretch, \(T_{1}\) at 1 K for the Si-H stretch in Si(100)-2×1:H is longer than 6 ns, while the corresponding value for the Si-D stretch in Si(100)-2×1:D is 250 ps. The values of \(\Omega\) for the Si-H and Si-D stretch are 2099 and 1530 cm\(^{-1}\), respectively. Similar to Si(111):H, energy relaxation for the Si(100):H system can only proceed via the pentatic interaction by a four-phonon process and is slow, while for the Si(100):D system, energy relaxation requires only three-phonon processes arising from the quartic interaction, and hence is considerably faster. It should be remarked that if the number of phonons participating in the relaxation process is large, the adiabatic approximation model may be more appropriate than the present perturbation approach.

Applying the theoretical results of this paper to analyze the experimental data of the C-H, C-D, Si-H and Si-D systems, we obtain \(\delta \omega_{0}, \gamma_{0}, \chi_{a}, \chi_{q}\) and \(A_{p}\) for these systems as listed in Table I. In principle, using the \textit{ab initio} calculation, we can determine the harmonic and anharmonic couplings given by Eqs. (17)–(21), which in turn can be used to obtain the spectral shifts, the spectral widths and spectral band-shapes. From Table I, we can see that the spectral shift \(\delta \omega_{0}\) is larger for C-H than for C-D. This can be understood from Eq. (24). Notice that

\[
c_{ii} = (\partial^{4}\hat{V}/\partial q_{i}^{2}\partial q_{i}^{2})_{eq}.
\]

The isotope effect in this case mainly originates from the derivative with respect to \(Q\) in Eq. (48). To a first approximation, we shall assume that \(Q\) is related to the adsorbate displacement \(\Delta x\) and the effective mass \(\mu\) by \(Q = \sqrt{\mu \Delta x}\). It follows that

\[
\frac{\Delta \omega_{CH}}{\Delta \omega_{CD}} = \frac{\Omega_{CH}}{\Omega_{CD}} c_{ii}(CH)/c_{ii}(CD) = \frac{\sqrt{\mu_{CH}}}{\mu_{CD}}.
\]

If we use the ratio of \(\mu_{CH}/\mu_{CD}\) as 2, then Eq. (49) gives \(\Delta \omega_{CH}/\Delta \omega_{CD} = \sqrt{2}\), agreeing with the data in Table I. In the case of Si(100):H and Si(100):D, \(\Delta \omega_{SIH}/\Delta \omega_{SIDS}\) is expected to be approximately given by \(\sqrt{2}\) as well.

Finally, throughout the discussions, we have assumed only homogeneous broadening of the spectra. The effect of inhomogeneity can be taken into account in the IR absorption spectra by rewriting Eq. (4) as

\[
\chi_{ij}(\omega) = \frac{2l}{\hbar} \sum_{mn} \sum_{n} \int_{0}^{\infty} \int_{0}^{\infty} \left(\frac{\partial \mu_{i}}{\partial Q_{j}}\right)_{m} \mid\langle n|Q_{i}\rangle_{m}\rangle^{2} \int_{0}^{\infty} dt \exp[-it(i(\omega_{mn} - \omega) + \Gamma_{mn})],
\]

and averaging this result over a distribution \(\mathcal{A}(\omega_{mn})\) of the transition frequencies. If \(\mathcal{A}(\omega_{mn})\) is a Gaussian distribution, it follows from Eq. (50) then that the lineshape function becomes a mixture of Lorentzian and Gaussian forms.

**VII. CONCLUSION**

In this paper we have presented a theory of the lineshape for the infrared absorption and the sum-frequency generation spectra for the adsorbate vibration. We employ the generalized master equation to describe the time evolution of the reduced density matrix of the adsorbate, and by calculating the damping operator to second order in the anharmonic interaction between the adsorbate and the substrate, we obtain the results for the line width and line shift in terms of the matrix elements of the anharmonic interaction. The line width consists of a dephasing and an inelastic contribution, and unlike previous analysis, \(\delta \omega_{0}\) it is not necessary to use different theories for each of these contributions. We then use a polynomial expansion of the anharmonic interaction in the adsorbate and substrate phonons coordinates, and derive relatively simple expressions under the quasi-mode approximation for the energy relaxation times, dephasing time, and the line shift. While the available data for the system C(111):H does not allow us to distinguish between the present and previous approaches, it is felt that our method has the advantage that it can readily be generalized to include higher order interactions for both the dephasing and energy relaxation simultaneously. Furthermore, approximations are introduced in Sec. V in order to obtain simple expressions to facilitate fitting the experimental data. When more accurate and extensive measurements become available, \textit{ab initio} calculation of the adsorbate-substrate interaction should be performed, and the general expressions for the line shift and the dephasing and energy relaxation times derived in Sec. IV can be used to compute accurate values of the lineshape parameters.

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