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SPECTRAL LINE SHAPE OF HIGH–FREQUENCY LOCAL VIBRATIONS IN ADSORBED MOLECULAR LATTICES

I. V. Kuzmenko[1], V. M. Rozenbaum[2]
Institute of Surface Chemistry National Academy of Sciences of Ukraine Prosp. Nauki 31, Kyiv-22, 252022 Ukraine

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We consider high–frequency local vibrations anharmonically coupled with low–frequency modes in a planar lattice of adsorbed molecules. The effect of lateral intermolecular interactions on the spectral line shape for local vibrations is analyzed in the limit of the high density of adsorbed molecules. It is shown that the spectral line positions and widths depend on behaviour of low–frequency distribution function for a system of adsorbed molecules. The results obtained allows the spectral line characteristics of the local vibrations for isotopically diluted $^{13}C^{16}O_2$ molecules in the $^{12}C^{16}O_2$ monolayer on the NaCl(100) surface to be described in agreement with the experimentally measured values.

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It is well known that the spectral line broadening for high–frequency local vibrations is caused by anharmonic coupling between high– and low–frequency modes [1–3]. At a sufficiently high frequency of the local vibrations, the dephasing model proved fruitful for description of vibrational spectra of adsorbed molecules [4–6], as it has afforded a number of exact solutions [7–9] and it has also allowed consideration of degenerate low–frequency deformation vibrations and their intrinsic anharmonicity [10]. If the amount of adsorbed molecules suffices to form a monolayer, the dephasing model should take into account collectivization of vibrational molecular modes [11–12]. The dephasing of collectivized high–frequency vibrations of adsorbates by low–frequency resonance molecular modes not interacting between themselves was studied in Ref. [11]. On the other hand, it is well known that forming of the lattices of inclined-oriented adsorbed molecules, e.g., CO and CO_2 systems on the NaCl(100) surface [15,16] causes the essential coupling for the low–frequency deformation modes of the adsorbates [12–14,17,18].

In the framework of the conventional exchange dephasing model, spectral line shift and width for a local vibration of a single adsorbed molecule are expressed in terms of the anharmonic coupling of this vibration with a translational or orientational molecular vibration with low frequency ω_ℓ. The last acquires a resonance nature due to its interaction with the quasicontinuous

[1]E-mail address: tanya@ap3.bitp.kiev.ua
[2]E-mail address: vrozen@mail.kar.net

spectrum of crystal lattice phonons [6,10]. For a planar molecular lattice only the collective low–frequency molecular modes with quasimoment $k < \omega_\ell / c_T$ (c_T is the transverse sound velocity) are damped via one–phonon emission [19]. If the density of adsorbed molecules is sufficiently high, i.e., provided the inequality

$$\frac{\omega_\ell^2}{4\pi n_a c_T^2} << 1 \tag{1}$$

is valid (n_a is the number of adsorbed molecules per unit area), energy of low–frequency vibration of a molecule is dissipated through lateral intermolecular interactions and interactions of the molecules with substrate are less important. To put it differently, the low–frequency vibration of a molecule decays by emission of vibrational modes of neighbouring molecules.

In this paper, we investigate dephasing of local vibrations for a system of anharmonically coupled high– and low–frequency molecular vibrations. It is shown that the experimentally observed spectra of the local vibrations in the planar lattices of adsorbed molecules can be described when lateral interactions between the low–frequency vibrations of the adsorbed molecules are considered. If translational symmetry is characteristic of the system, the harmonic parts of its Hamiltonian can be introduced in a diagonal form with respect to the two–dimensional wave vector $\mathbf{k}$ belonging to the first Brillouin zone of the planar lattice [18]. Then we represent total Hamiltonian as a sum of harmonic and anharmonic contributions:

$$H = H_0 + H_A, \tag{2}$$

$$H_0 = \hbar\Omega_h \sum_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} b_{\mathbf{k}}^+ b_{\mathbf{k}}, \tag{3}$$

$$H_A = \frac{\hbar\gamma}{N} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} a_{\mathbf{k}}^+ a_{\mathbf{k}'} b_{\mathbf{k}''}^+ b_{\mathbf{k}-\mathbf{k}'+\mathbf{k}''}, \tag{4}$$

where $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^+$ ($b_{\mathbf{k}}$ and $b_{\mathbf{k}}^+$) are annihilation and creation operators for the molecular vibrations of the high frequency Ω_h (low frequency $\omega_{\mathbf{k}}$), γ is the biquadratic anharmonicity coefficient, N is the number of molecular lattice sites in the main area. Other types of anharmonic coupling do not contribute to the spectral line broadening [3–5] with the exception of additionally renormalizing the biquadratic anharmonicity coefficient [20,21], so that the model in question is widely involved in the interpretation of experimental spectra by fitting the parameter values.

In the low–temperature limit ($k_B T << \hbar\omega_{\mathbf{k}}$) the spectral line for high–frequency molecular vibrations is of the Lorentz–like shape with the shift of its maximum $\Delta\Omega$ and width 2Γ are defined by the following relationships [17]:

$$\begin{pmatrix} \Delta\Omega \\ 2\Gamma \end{pmatrix} = \begin{pmatrix} \mathrm{Re} \\ -2\mathrm{Im} \end{pmatrix} W, \tag{5}$$

$$W = \frac{\gamma}{N} \sum_{\mathbf{k}} n(\omega_{\mathbf{k}}) \left[1 - \frac{\gamma}{N} \sum_{\mathbf{k}'} \frac{1}{\omega_{\mathbf{k}} - \omega_{\mathbf{k}'} + i0} \right]^{-1}, \tag{6}$$

where $n(\omega) = \left[e^{\beta\hbar\omega} - 1 \right]^{-1}$ is the Bose–factor, $\beta = (k_B T)^{-1}$.

The spectral characteristics described by expressions (4) and (5) are determined by certain function of lateral interaction parameters and of the anharmonicity coefficient γ. Assuming that low–frequency molecular band is sufficiently narrow, that is, the inequality $\beta\hbar\Delta\omega << 1$ is valid, and substituting $n(\omega_\ell)$ for $n(\omega)$ in expression (5), the equation considered takes the form:

$$W = \gamma n\left(\omega_\ell\right) \int\limits_{-\infty}^{\infty} \frac{\varrho(\omega) d\omega}{1 - \gamma \int\limits_{-\infty}^{\infty} \varrho(\omega') d\omega' \left[\omega - \omega' + i0\right]^{-1}}, \tag{7}$$

where

$$\varrho(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \delta(\omega - \omega_{\mathbf{k}}) \tag{8}$$

is the low–frequency distribution function for a molecular lattice.

To investigate the lateral interaction effect on basis spectral characteristics of high–frequency vibrations, assume that the anharmonicity coefficient γ is sufficiently small. Expanding W in powers of γ and retaining the terms of the orders γ and γ^2, we derive the following expressions for spectral line shift and width:

$$\Delta\Omega = \gamma n(\omega_\ell), \tag{9}$$

$$2\Gamma = \frac{2\pi\gamma^2}{\eta_{\text{eff}}} n(\omega_\ell), \tag{10}$$

where

$$\eta_{\text{eff}} = \left[\int\limits_{-\infty}^{\infty} \varrho^2(\omega) d\omega\right]^{-1}. \tag{11}$$

Equations (8) and (9) express the spectral line shift and width in terms of the anharmonic coefficient γ and the parameter η_{eff}. The last characterizes lateral interactions of low–frequency molecular vibrations. Lateral interactions cause the molecular vibrations to collectivize, that is, a molecular vibration with the frequency ω_ℓ transforms into a band of collective vibrations in an adsorbed molecular lattice with nonzero band width $\Delta\omega$. Then assuming that the frequency ω_ℓ is located at the centre of the vibrational band, the distribution function (7) can be represented as:

$$\varrho(\omega) = \begin{cases} \Delta\omega^{-1} f(z), & |\omega - \omega_\ell| < \Delta\omega/2 \\ 0, & |\omega - \omega_\ell| > \Delta\omega/2 \end{cases} \tag{12}$$

$(z = (\omega - \omega_\ell)/\Delta\omega)$ with the dimensionless function $f(z)$ determined by the dispersion law for the low–frequency molecular vibrations. By virtue of the fact that the distribution function (7) is normalized to unity, the following equation is valid:

$$\int\limits_{-1/2}^{1/2} f(z) dz = 1. \tag{13}$$

For η_{eff} (10) to be calculated, consideration must be given to specific dispersion laws for vibrations induced by anisotropic intermolecular interactions. However the contribution of lateral interactions to spectral characteristics is frequently described by a single parameter, the band width $\Delta\omega$ for collectivized vibrations of adsorbates, with function $f(z)$ assumed to be equal to the step function $\theta\left(1-4z^2\right)$. Then Eq. (10) takes the form:

$$\eta_{\text{eff}}^{(0)} = \Delta\omega. \tag{14}$$

Taking account of the distribution function peculiarities leads to the change in the parameter η_{eff}. Since the function $f(z)$ is normalized by Eq. (12), the expression (10) can be rewritten as:

$$\eta_{\text{eff}} = \eta_{\text{eff}}^{(0)} \left[1 + \int\limits_{-1/2}^{1/2} \left(f(z)-1\right)^2 dz\right]^{-1}. \tag{15}$$

Eq. (14) evidently demonstrate the decrease in the parameter η_{eff} if the distribution function differs from the step function.

To estimate the parameter η_{eff} let us assume the circular first Brillouin zone, $0 < k < k_{\text{max}}$ ($k_{\text{max}} = \sqrt{4\pi n_a}$) and approximate the dispersion law for low–frequency vibrations by the following expression:

$$\omega_{\mathbf{k}} = \omega_\ell - \frac{\Delta\omega}{2}\left[1 - 2\left(1-a\right)\frac{k}{k_{\text{max}}} + 2a\left(\frac{k}{k_{\text{max}}}\right)^2\right], \tag{16}$$

with the arbitrary parameter a ($|a| < 1$). The relationship (15) involves the linear in k term, which is in agreement with the dispersion laws for two–dimensional lattice systems constituted by dipole moments [14]. Substituting the expression (15) into Eq. (7) and integrating derived relation with respect to wave vector $\mathbf{k}$ we obtain the dimensionless distribution function:

$$f(z) = \frac{1}{a}\left[\frac{1+a}{\left[(1+a)^2 - 2a(2z+1)\right]^{1/2}} - 1\right], \quad |z| < \frac{1}{2}. \tag{17}$$

At $a = -1$ the function (16) reduces to the step function $\theta\left(1-4z^2\right)$. Substitution of the expression (16) into Eq. (10) gives:

$$\eta_{\text{eff}} = \Delta\omega a^2 \left[\frac{1+a}{2a}\ln\frac{1+a}{1-a} - 1 - 2a\right]^{-1}. \tag{18}$$

Parameter η_{eff} varies from $\Delta\omega$ at $a = -1$ to zero at $a = 1$. At $a = 0.8$ (which is consistent with the realistic dispersion laws):

$$\eta_{\text{eff}} = 0.34\Delta\omega. \tag{19}$$

In what follows we consider relationship (6) (which is true for arbitrary values of γ and $\eta_{\rm eff}$), with the density of states for the low–frequency band approximated by the step function with the step width $\eta_{\rm eff}$. Then Eq. (6) takes the form:

$$W = \gamma n\left(\omega_\ell\right) \int\limits_{-1/2}^{1/2} dz \left[1 - \frac{\gamma}{\eta_{\rm eff}} \ln \frac{1+2z}{1-2z} - \frac{i\pi\gamma}{\eta_{\rm eff}}\right]^{-1} . \qquad (20)$$

The expression (19) allows the lateral interaction parameters to be determined by a comparison between observed and calculated spectral characteristics.

An example of adsorbed lattices with strong lateral interactions is the system of isotopically diluted $^{13}C^{16}O_2$ molecules in the $^{12}C^{16}O_2$ monolayer on the NaCl(100) surface. Stretch vibration frequencies for $^{13}C^{16}O_2$ and $^{12}C^{16}O_2$ molecules differ by 60 cm^{-1} and their coupling can thus be neglected. In contrast, low–frequency vibrations prove to be essentially coupled. As far as translational vibrations are concerned, the mass difference between carbon isotopes is slight compared to the total molecular mass, whereas for orientational vibrations, the mass of the central carbon atom has only a slight effect on the molecular moment of inertia. Temperature dependent shift and width of spectral line of stretch vibrations with the frequency $\Omega_h = 2281.6\ \mathrm{cm}^{-1}$ at $T = 1$ K [22] can be approximated in the range from $T = 1$ K to 80 K by the following expressions:

$$\Delta\Omega = 0.52 n(\omega_\ell)\ \mathrm{cm}^{-1}, \qquad (21)$$

$$2\Gamma = 0.61 n(\omega_\ell)\ \mathrm{cm}^{-1}, \qquad (22)$$

and $\omega_\ell = 41\ \mathrm{cm}^{-1}$. To explain observed spectral characteristics we equate expressions (20) and (21) with the real and imaginary parts of the W (19) and obtain two equations in two parameters: γ and $\eta_{\rm eff}$. Solving this system of equations we have the following parameter values: $\gamma = 0.78\ \mathrm{cm}^{-1}$ and $\eta_{\rm eff} = 3.8\ \mathrm{cm}^{-1}$. Using Eq. (18) we obtain the value of effective band width for the low–frequency vibrations: $\Delta\omega = 11\ \mathrm{cm}^{-1}$, which is in good agreement with the band width for collectivized orientational vibrations of CO_2 molecules with quadrupole–quadrupole intermolecular interactions.

We note in conclusion that attempts to describe the temperature dependences of the spectral line shape for the above-mentioned CO_2 molecular ensemble in the framework of the conventional exchange dephasing model for a single adsorbed molecule lead to overestimated spectral line width, whereas calculated line shift agrees well with experimental values. Taking into consideration the lateral interactions between the low–frequency vibrations of the adsorbates, the model advanced provides agreement between calculated and observed spectral line shift and width.

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