DEPHASING OF LOCAL VIBRATIONS IN A PLANAR LATTICE OF ADSORBED MOLECULES

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We investigate anharmonically coupled high– and low–frequency excita-
tions in a planar lattice of adsorbed molecules interacting with phonons of a
crystal. Dephasing of high–frequency local vibrations by low–frequency res-
onance modes is described in terms of temperature Green’s function. The
equations obtained are solved, first, with a small ratio of the anharmonic cou-
pling coefficient for high– and low–frequency modes to the resonance width,
and second, in the low–temperature limit. High–frequency spectral line posi-
tions and widths depend on dispersion laws and resonance mode lifetimes. It is
shown that lateral interactions of low–frequency modes of adsorbed molecules
can lead to a significant narrowing of high–frequency spectral lines, which is
consistent with experimental data.

A considerable progress in the understanding of the broadening mechanism for a high–
frequency local vibration spectral line of an impurity molecule has been achieved due to
studies on the self-scattering (dephasing) of this vibration arising from a biquadratic anhar-
monic coupling between high– and low–frequency molecular modes [1–3]. At a sufficiently
high frequency of the local vibration, other anharmonic coupling types do not contribute
to the spectral line broadening [3–5] with the exception of additionally renormalizing the
biquadratic anharmonicity coefficient [6]. In this context, of significance is that the low–

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frequency mode acquires a resonance nature due to its interaction with the quasicontinuous spectrum of crystal lattice phonons. In the treatment of the self-scattering effect, the dephasing model [4,7,8] proved fruitful, as it afforded a number of exact solutions [9–12] and hence a description of spectral line shapes for local vibrations.

If the amount of adsorbed molecules suffices to form a monolayer, the dephasing model should take into account collectivization of vibrational molecular modes [13–16]. As a rule, high– and low–frequency lattice excitations are respectively related to stretch and deformation (translational or orientational) molecular vibrations.

In this paper, a dephasing model for local vibrations is investigated for a system of anharmonically coupled high– and low–frequency molecular vibrations, with crystal phonons included. If translational symmetry is characteristic of the system considered, the low–frequency contribution to 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 a planar lattice [17]. Then the total Hamiltonian is written as a sum of harmonic and anharmonic contributions:

$$ H_{\text{tot}} = H + H_A, \quad H = \sum_{\mathbf{K}} H_{\mathbf{K}}, $$

$$ H_{\mathbf{K}} = \hbar \Omega_{\mathbf{K}} a_{\mathbf{K}}^\dagger a_{\mathbf{K}} + \hbar \omega_{\mathbf{K}} b_{\mathbf{K}}^\dagger b_{\mathbf{K}} + \hbar \sum_{\nu} \omega_{\mathbf{K},\nu} \beta_{\mathbf{K},\nu}^\dagger \beta_{\mathbf{K},\nu} + \hbar \sum_{\nu} (\chi_{\mathbf{K},\nu} b_{\mathbf{K}}^\dagger \beta_{\mathbf{K},\nu} + \text{H.c.}), $$

$$ H_A = \frac{\hbar \gamma}{N} \sum_{\mathbf{K}\mathbf{K}'} a_{\mathbf{K}}^\dagger a_{\mathbf{K}}' b_{\mathbf{K}}^\dagger b_{\mathbf{K}'+\mathbf{K}'}^\dagger, $$

where the terms in the expression (2) respectively represent high– and low–frequency vibrations of a molecular lattice, crystal phonons, and the harmonic interactions between phonons and low–frequency modes. In the above relation, quantum states of phonons of the admolecular lattice are characterized by the surface–parallel wave vector $\mathbf{K}$, whereas the quantum numbers of substrate phonons are indicated by the couple of indices $\mathbf{K}$ and $\nu$. The latter accounts for the polarization of a quasi–particle and its motion in the surface–normal direction; it implicitly reflects both the atomic arrangement in the crystal unit cell and the...
position of the admolecular lattice, as a whole, relative to the crystal surface. The utility of introduction of the complex index $\nu$ was substantiated previously [17].

As a rule, the density of states for molecular lattice vibrations is negligible as compared to that for crystal phonons. Therefore, the $\mathbf{K}$–mode of a molecular lattice interacts with the crystal phonons specified by the same wave vector $\mathbf{K}$. Besides, the low–frequency collective mode $\omega_\mathbf{K}$ of adsorbed molecules can be considered as a resonance vibration with the renormalized frequency $\tilde{\omega}_\mathbf{K}$ and the inverse lifetime $\eta_\mathbf{K} (\tilde{\omega}_\mathbf{K})$ [12,17].

The response of the system concerned to an external electromagnetic field is conveniently described in terms of double-time Green’s function (GF) which can be introduced in a variety of representations [18–22]. In what follows we will involve the representation in Matsubara’s frequency space [18] which is accepted in the theory of anharmonic crystals [23] and provides a number of exact solutions in the case of a single adsorbed molecule [10,11]. In this approach, the spectral line shape for high–frequency vibrations can be determined as follows:

$$L(\omega) = \frac{\hbar \beta}{\pi} \text{Im} G(a_0 a_0^+, \omega), \quad \beta = (k_B T)^{-1},$$  \hspace{1cm} (4)

$$G(a_0 a_0^+, \omega) = \frac{1}{\beta} \int_{-\infty}^{+\infty} d\tau G(a_0 a_0^+, \tau) e^{i \omega \tau},$$  \hspace{1cm} (5)

$$G(a_0 a_0^+, \tau) = \frac{\langle \hat{\tau} \hat{a}_0(\tau) \hat{a}_0^+(0) \hat{S}(\beta) \rangle_0}{\langle \hat{S}(\beta) \rangle_0},$$  \hspace{1cm} (6)

where

$$\hat{S}(\beta) = \hat{S}(\beta, 0),$$

$$\hat{S}(\tau, \tau_0) = \hat{\tau} \exp \left[ - \int_{\tau_0}^{\tau} d\tau' \hat{H}_A(\tau') \right],$$  \hspace{1cm} (7)

$$\hat{A} = e^{\hat{H} \tau} \hat{A} e^{-\hat{H} \tau}, \quad \langle \ldots \rangle_0 = \frac{\text{Sp} \{ e^{-\beta \hat{H}} \ldots \} }{\text{Sp} \{ e^{-\beta \hat{H}} \} },$$  \hspace{1cm} (8)
and \( \hat{A} \) is an arbitrary operator function.

Expanding the right side of Eq. (6) in powers of the anharmonic coupling coefficient \( \gamma \), the temperature GF (6) is expressed in terms of the GF’s of high- and low-frequency vibrations of a planar lattice in the harmonic approximation:

\[
G^{(0)}_K(\tau) = \langle \hat{r}a_K(\tau)a_K^+(0) \rangle_0 = \left\{ [n(\Omega_K) + 1]\theta(\tau) + n(\Omega_K)\theta(-\tau) \right\} \exp(-\hbar\Omega_K\tau), \tag{9}
\]

\[
g^{(0)}_K(\tau) = \langle \hat{r}b_K(\tau)b_K^+(0) \rangle_0 = \int d\omega \Re K(\omega) \left\{ [n(\omega) + 1]\theta(\tau) + n(\omega)\theta(-\tau) \right\} \exp(-\hbar\omega\tau), \tag{10}
\]

where

\[
n(\omega) = \left[ e^{\beta\hbar\omega} - 1 \right]^{-1} \tag{11}
\]

is the Bose-factor and

\[
\Re K(\omega) = \frac{\bar{\eta}_K(\omega)}{\left( \omega - \omega_K - \bar{P}_K(\omega) \right)^2 + \pi^2\bar{\eta}_K^2(\omega)} \tag{12}
\]

is the resonance spectral function of low-frequency vibrations \([12,24]\),

\[
\bar{\eta}_K(\omega) = \sum_{\nu} |\chi_{K,\nu}|^2 \delta(\omega - \omega_{K,\nu}), \quad \bar{P}_K(\omega) = \int_{-\infty}^{\infty} \frac{\bar{\eta}_K(\bar{\omega})d\bar{\omega}}{\omega - \bar{\omega}}. \tag{13}
\]

The real and imaginary parts of the pole in expression (12) define the renormalized frequency \( \tilde{\omega}_K \) and the inverse lifetime \( \eta_K = 2\pi\bar{\eta}_K(\tilde{\omega}_K) \) of the resonance vibration.

Let us take advantage of the inequality \( \beta\hbar\Omega_K >> 1 \) permitting neglect of the terms of the order \( \exp(-\beta\hbar\Omega_K) \). Then the trace taken over high- and low-frequency modes, \( \text{Sp}\{...\} \), is reduced to that for low-frequency modes, with all high-frequency vibrations considered only for the ground state. The resulting temperature GF (6) takes the form:

\[
G(a_0a_0^+, \tau) = \langle \tilde{a}_0(\tau)\tilde{S}(\tau)\tilde{a}_0^+(0) \rangle_0, \quad \beta > \tau > 0. \tag{14}
\]
Thus, provided the inequality $\beta \hbar \Omega_K >> 1$ is valid, the GF defined above can be written in the form involving no high–frequency mode operators:

$$G(a_0^+a_0^0, \tau) = \exp (\hbar \Omega_0 \tau) \langle \hat{s}_{00}(\tau) \rangle_0,$$

(15)

$$\hat{s}_{KK'}(\tau) = \sum_{n=0}^{\infty} (\hbar \gamma)^n \int_0^\tau \! \! d\tau_1 \ldots \int_0^{\tau_{n-1}} \! \! d\tau_n \sum_{K_1 \ldots K_{n-1}} \tilde{B}_{KK_1}(\tau_1) \tilde{B}_{K_1K_2}(\tau_2) \ldots \tilde{B}_{K_{n-1}K'}(\tau_n),$$

(16)

$$\tilde{B}_K(\tau) = \frac{1}{N} \exp [\hbar (\Omega_K - \Omega_{K'})] \sum_{K'} b_{K'K}(\tau) b_{K'K'}(\tau).$$

(17)

Representing average value (15) as

$$\langle \hat{s}_{00}(\tau) \rangle_0 = e^{F(\tau)}$$

(18)

and differentiating the left and the right sides of expression (18) with respect to $\tau$, we arrive at:

$$\frac{dF(t)}{dt} = -\hbar \gamma \sum_{K} \frac{\langle \tilde{B}_{0K}(\tau) \hat{s}_{00}(\tau) \rangle_0}{\langle \hat{s}_{00}(\tau) \rangle_0}.$$  

(19)

Eq. (19) allows the line shape to be determined in the approximation of the small anharmonic coefficient $\gamma$, as well as in the low–temperature limit.

Importantly, the three-time GF

$$g_{KK'}(\tau, \tau', \tau'') = \frac{\langle \hat{\tau} \tilde{b}_K(\tau) b_{K'}^{+}(\tau') \hat{s}_{K-K',0}(\tau'') \rangle_0}{\langle \hat{s}_{00}(\tau) \rangle_0}$$

(20)

satisfies the Dyson–like equation with the assumption of non–interacting high–frequency collective vibrations ($\Omega_K = \Omega_0$):

$$g_{KK'}(\tau, \tau', \tau'') = g_{K}^{(0)}(\tau - \tau') \delta_{KK'} + \frac{\hbar \gamma}{N} \sum_{K_1} \int_0^{\tau''} \! \! d\tau_1 g_{K}^{(0)}(\tau - \tau_1) g_{K_1K'}(\tau_1, \tau', \tau'').$$

(21)

(the resonance GF $g_{K}^{(0)}(\tau)$ in the harmonic approximation is determined by the expression (10)). Equation (21) takes into account intermolecular interactions of low–frequency resonance modes and thus generalizes the corresponding equations derived in papers [10,11].
To invoke the perturbation theory for small anharmonic coupling coefficient, we use the Wick theorem for the coupling of the creation and annihilation operators of low–frequency modes in expression (19). Retaining the terms of the orders $\gamma$ and $\gamma^2$ we are led to the following expressions for the shift $\Delta \Omega$ and the width $2\Gamma$ of the high–frequency vibration spectral line:

$$\Delta \Omega = \frac{\gamma}{N} \sum_K \int_{-\infty}^{\infty} d\omega n(\omega) R_K(\omega),$$  \hspace{1cm} (22)

$$2\Gamma = \frac{2\pi \gamma^2}{N^2} \sum_{KK'} \int_{-\infty}^{\infty} d\omega n(\omega) R_{K+K'}(\omega) R_{K'}(\omega + \Omega_0 - \Omega_K),$$ \hspace{1cm} (23)

where $n(\omega)$ and $R_K(\omega)$ are respectively determined by relations (11) and (12). It should be noted that expressions (22) and (23) describe a single Lorentz–like spectral line of local vibrations, with its position and width dictated by dispersion laws and lifetimes for resonance low–frequency modes.

The analytical description of high–frequency line shapes becomes possible in the low–temperature limit, i.e., at $n(\omega_K) \approx \exp(-\beta \hbar \omega_K) << 1$, which represents an experimentally important case. In this situation, the Wick coupling for the operators of low–frequency modes in expression (19) involves only the terms in which the annihilation operator is to the left of the creation operator in all but one operator pair. Then Eq. (19) can be written as:

$$\frac{dF(\tau)}{d\tau} = -\frac{\hbar \gamma}{N} \sum_K d\omega R_K(\omega) n(\omega) \sum_{n=0}^{\infty} (-\hbar \gamma)^n \int_0^\tau d\tau_1 \varphi_K(\omega, \tau - \tau_1)$$

$$\times \int_0^{\tau_1} d\tau_2 \varphi_K(\omega, \tau_2 - \tau_1) \ldots \int_0^{\tau_{n-1}} d\tau_n \varphi_K(\omega, \tau_n - \tau_1) \hspace{1cm} (24)$$

where

$$\varphi_K(\omega, \tau) = \frac{1}{N} \sum_{K'} \int_{-\infty}^{\infty} d\omega' \exp \left[ \hbar (\Omega_0 - \Omega_{K-K'} + \omega - \omega') \tau \right]$$

$$\approx \frac{1}{N} \sum_{K'} \exp \left[ \hbar (\Omega_0 - \Omega_{K-K'} + \omega - \omega_K + i\pi \tilde{\gamma}(\omega_K)) \tau \right] \hspace{1cm} (25)$$

On integrating Eq. (24) over the variables $\tau_1, \tau_2, \ldots, \tau_n$, we obtain:
\[
\frac{dF(\tau)}{d\tau} = -\frac{\hbar\gamma}{2\pi N} \sum K \int_{-\infty}^{\infty} d\omega \mathbb{R}_K(\omega)n(\omega) \int_{-\infty}^{\infty} dy e^{\tau(\lambda + iy)} \\
\times \left[ 1 + \hbar\gamma \int_{-\infty}^{\infty} \varphi_K(\omega, x) e^{-\tau(\lambda + iy)} \right]^{-1}.
\]  \tag{26}

Then expression (26) in the Markov approximation \([\hbar \tilde{\eta}_K(\omega), \hbar \gamma \tau >> 1]\) can be reduced as follows:

\[
\frac{dF(\tau)}{d\tau} = -\frac{\hbar\gamma}{N} \sum K \frac{n(\omega_K)}{1 - (\gamma/N) \sum K' \{ \alpha_{KK'} + i\pi [\tilde{\eta}_K(\omega_K) + \tilde{\eta}_{K'}(\omega_{K'})] \}^{-1}}, \tag{27}
\]

where

\[
\alpha_{KK'} = \Omega_0 - \Omega_K - K' + \omega_K - \omega_{K'}. \tag{28}
\]

As seen, the spectral line of high–frequency local vibrations is of the Lorentz–like shape:

\[
L(\omega) = -\frac{1}{\pi} \text{Im} \frac{1}{\omega - \Omega_0 - W}, \quad W = -\frac{dF(\tau)}{d\tau}, \tag{29}
\]

with the shift \(\Delta \Omega = \text{Re}W\) and the width \(2\Gamma = -2\text{Im}W\).

To estimate the lateral interaction effect on basic spectral characteristics of high–frequency local vibrations, assume that the density of states for the low–frequency band is described by the step function:

\[
\rho_\varphi(\omega) = \begin{cases} \\
\Delta \omega^{-1}, & \omega_0 < \omega < \omega_0 + \Delta \omega, \\
0, & \text{otherwise}.
\end{cases} \tag{30}
\]

with the step width \(\Delta \omega\), which is normally much greater than the width of the high–frequency vibration band. In addition, suppose resonance widths \(\eta_K(\omega)\) to be much the same on the interval \(\Delta \omega\) \([\eta_K(\omega) \approx \eta_K(\omega_0) \equiv \eta]\). Then, relation (27) takes the form:

\[
W = \frac{\gamma e^{-\hbar \omega_0/k_BT}}{\Delta \Omega} \int_0^{\Delta \omega} dx e^{-\hbar x/k_BT} \left( 1 + \frac{\gamma}{\Delta \Omega} \ln \frac{x + i\eta - \Delta \omega}{x + i\eta} \right)^{-1}. \tag{31}
\]

Assuming the sufficiently small ratio \(\Delta \omega/\eta\) and allowing for the fact that the quantities \(\Delta \Omega\) and \(2\Gamma\) essentially differ from zero only when \(k_BT\) approaches \(\omega_0\) (i.e., provided the...
inequalities $\Delta \omega \ll \eta \ll k_B T / \hbar < \omega_0$ hold), we obtain, accurate to terms of the orders $\Delta \omega / T$ and $(\Delta \omega / \eta)^2$:

$$\Delta \Omega \approx \frac{\gamma \eta^2}{\gamma^2 + \eta^2} \left[ 1 - \frac{\hbar \Delta \omega}{2 k_B T} + \frac{\gamma^2 (9 \gamma^2 + 13 \eta^2)}{12 (\gamma^2 + \eta^2)^2} \left( \frac{\Delta \omega}{\eta} \right)^2 \right] e^{-\hbar \omega_0 / k_B T},$$ (32)

$$2 \Gamma \approx \frac{2 \gamma^2 \eta}{\gamma^2 + \eta^2} \left[ 1 - \frac{\hbar \Delta \omega}{2 k_B T} - \frac{6 \eta^4 - 3 \gamma^2 \eta^2 - 5 \gamma^4}{12 (\gamma^2 + \eta^2)^2} \left( \frac{\Delta \omega}{\eta} \right)^2 \right] e^{-\hbar \omega_0 / k_B T}.$$ (33)

At $\Delta \omega = 0$, relations (32) and (33) are reduced to the reported results [8] for an adsorbed molecule. Lateral interactions of adsorbed molecules give rise to the low–frequency molecular band with the non–zero parameter $\Delta \omega$. The integration over this band leads to the decreased shift and width of the high–frequency spectral line. Since the parameters $\hbar \Delta \omega / k_B T$ and $(\Delta \omega / \eta)^2$ in the temperature range of interest can be of the same order of magnitude, the contribution $(\Delta \omega / \eta)^2$ to the value $\Delta \Omega$ can be only positive, whereas the sign of this contribution to the value $2 \Gamma$ depends on the $\eta$ to $\gamma$ ratio. At $\eta / \gamma > 1.094$ (which is consistent with the realistic values of $\eta$ and $\gamma$), the contribution $(\Delta \omega / \eta)^2$ causes the additional narrowing of the spectral line.

Table 1 shows temperature dependences of the high–frequency line shift and width, with the parameter values corresponding to isotopically diluted $^{13}$C$^{16}$O$_2$ molecules in the $^{12}$C$^{16}$O$_2$ monolayer on the NaCl(100) surface [25]. The data outlined are indicative of changes in spectral line shifts and widths when passing from the band width $\Delta \omega = 5$ cm$^{-1}$ to $\Delta \omega = 0$. These dependences evidently demonstrate the narrowing of the spectral line, in accordance with experimental results [25]. In the framework of the conventional exchange dephasing model, i.e., with no regard to lateral interactions of low–frequency modes, an attempted description of the temperature dependences for the above-mentioned $^{13}$C$^{16}$O$_2$ molecular ensemble resulted in overestimated line widths, whereas theoretically calculated line shifts agreed well with experimental values. 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. With the coupling of low-frequency vibrations included, the model suggested provides an accordance between calculated and observed spectral line widths.

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Table 1. Temperature dependences of the spectral line shift (a) and width (b) for molecular local vibrations, with intermolecular interactions neglected ($\Delta\omega = 0$) and included ($\Delta\omega = 5$ cm$^{-1}$) for the following parameter values: $\gamma = 0.7$ cm$^{-1}$, $\eta = 1.2$ cm$^{-1}$, $\omega_0 = 41$ cm$^{-1}$.

(a)

| T (K) | $\Delta\Omega$ (cm$^{-1}$) at $\Delta\omega = 0$ | $\Delta\Omega$ (cm$^{-1}$) at $\Delta\omega = 5$ cm$^{-1}$ |
|-------|---------------------------------|---------------------------------|
| 20    | 0.027223                        | 0.029096                        |
| 30    | 0.072878                        | 0.082131                        |
| 40    | 0.119241                        | 0.138051                        |
| 50    | 0.160221                        | 0.188547                        |
| 60    | 0.195096                        | 0.232113                        |
| 70    | 0.224566                        | 0.269276                        |
| 80    | 0.249553                        | 0.301008                        |

(b)

| T (K) | $2\Gamma$ (cm$^{-1}$) at $\Delta\omega = 0$ | $2\Gamma$ (cm$^{-1}$) at $\Delta\omega = 5$ cm$^{-1}$ |
|-------|---------------------------------|---------------------------------|
| 20    | 0.031761                        | 0.016631                        |
| 30    | 0.085025                        | 0.046801                        |
| 40    | 0.139113                        | 0.078537                        |
| 50    | 0.186925                        | 0.107158                        |
| 60    | 0.227612                        | 0.131831                        |
| 70    | 0.261993                        | 0.152864                        |
| 80    | 0.291145                        | 0.170817                        |