BAND EFFECT IN VIBRATIONAL DEPHASING OF ADATOMS BOUND TO SURFACE BY CENTRAL FORCES

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Abstract

The effect of lateral interactions of adatoms on the spectral line of their local vibrations is analyzed in terms of a simple model which includes only central forces binding adatoms to a surface, so that in a case free of lateral interactions the contribution from the surface-longitudinal vibrational mode to the dephasing process should vanish (K. Burke, D. C. Langreth, M. Persson, Z.-Y. Zhang, Phys. Rev. B 47 (1993) 15869). The lateral interactions are shown to cause the spectral line shift and broadening which are proportional to the cubed and the squared ratio of the band width for collectivized local vibrations to the resonance width for the longitudinal mode; as a result, band effect causes a notable contribution, provided this ratio is of order of unity.

To date a great variety of adsorbate systems have been investigated in which lateral dipole-dipole interactions not only manifest themselves in vibrational spectra [1] but also give rise to complex orientational structures [2-4]. A challenge given much space in the literature is to analyze the contribution of lateral interactions into the spectral line shift and broadening for local vibrations [5-8]. Up to now, attacking the problem has involved the exchange dephasing model with the biquadratic coefficient of the anharmonic coupling between the high-frequency local vibration and the low-frequency resonance mode responsible for temperature dependences of observed spectral lines. Noteworthy is that this approach included lateral interactions both for high-frequency [5] and low-frequency modes [6-8].

At the same time, consideration of a simpler case, isolated adatoms and admolecules, revealed a significant role of the cubic anharmonicity whose contribution to the dephasing is comparable to that of the biquadratic anharmonicity [9,10]. Given proper weight in the treatment of the dephasing process, this factor allowed to adequately account for the anharmonic coupling between the surface-transverse local mode and the surface-longitudinal resonance mode. Unlike the case of two identically oriented modes which are coupled even in the harmonic approximation and thus give rise to a reduction factor quenching the dephasing by several orders of magnitudes [11], two mutually perpendicular modes could be expected to cause a material effect. However, the binding of an adatom to a surface by central forces gives no contribution to the dephasing process, and only weaker non-central forces prevent it from vanishing at all [10]. Since additional lateral interactions of local modes in a sense represent non-central forces, an intriguing situation results, when the band effect can be investigated in its pure form, as it should merely be absent for not interacting adatoms. In the present contribution, we aim at the consideration of this pure effect and its contribution to the dephasing process in planar lattices of interacting adatoms.

We start from the Hamiltonian of a system of two mutually perpendicular modes $u_\perp$ and $u_\parallel$, presented in Ref. [10]:

$$H_\mathbf{R} = \frac{1}{2m}\left(p_\perp^2 + p_\parallel^2\right) + \frac{1}{2}m\omega_\parallel^2 u_\parallel^2 + U(l - l_0) \tag{1}$$

with the potential of central forces

$$U(r) = \Phi_2 r^2 + \Phi_3 r^3 + \Phi_4 r^4, \quad \Phi_2 = \frac{1}{2}m\Omega_\perp^2, \tag{2}$$

where

$$r \equiv l - l_0 = \sqrt{(l_0 + u_\perp)^2 + u_\parallel^2} - l_0 \approx u_\perp + \frac{1}{2l_0}u_\parallel^2 - \frac{1}{2l_0^2}u_\perp u_\parallel^2 \tag{3}$$

(l_0 is the equilibrium distance between the adatom and the surface atom bound to it, m is the reduced mass, $\Omega_\perp$ and $\omega_\parallel$ are the frequencies of the local and the resonance modes, with $\Omega_\perp \gg \omega_\parallel$, which is usually the case if adatom is small in mass). The potential of the anharmonic coupling between the two modes, when expanded in a power series in $u_\perp$ and $u_\parallel$ up to the term of the fourth degree appears as

$$U_{anh} = \Phi_4^\parallel u_\parallel^2 u_\perp^2 + \Phi_3^\parallel u_\parallel^2 u_\perp + \Phi_4^\perp u_\perp^4 + \Phi_3^\perp u_\perp^3 \tag{4}$$

and is characterized by the coefficients

$$\Phi_4^\parallel = \frac{1}{2l_0^2}(3\Phi_3 l_0 - 2\Phi_2), \quad \Phi_3^\parallel = \frac{1}{l_0}\Phi_2, \quad \Phi_4^\perp = \Phi_4, \quad \Phi_3^\perp = \Phi_3. \tag{5}$$

Lateral interactions between adatoms forming a planar lattice result in a band of collectivized local modes which is described in the harmonic approximation by the Hamiltonian [6,7,12]

$$H_\perp = \frac{1}{2}\sum_\mathbf{k}\left[|\widetilde{p}_\perp(\mathbf{k})|^2 + \Omega_\mathbf{k}^2|\widetilde{u}_\perp(\mathbf{k})|^2\right]. \tag{6}$$

Here the dispersion law $\Omega_\mathbf{k}$ is specified by the frequency $\Omega_\perp$ and parameters of dipole-dipole interaction:

$$\Omega_\mathbf{k}^2 = \Omega_\perp^2 + \frac{1}{m}\left(\frac{\partial\mu}{\partial u_\perp}\right)_0^2\sum_\mathbf{R}\frac{\exp(-i\mathbf{k}\cdot\mathbf{R})}{R^3} \tag{7}$$

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with μ and $\mathbf{R}$ respectively denoting the dipole moment and the radius vector of the two-dimensional lattice.

Ref. [13] reported the relations of interest to us which defined the shift and the halfwidth of the spectral line for collectivized local vibrations and were deduced using the fourth-order perturbation theory in all possible cubic and quartic anharmonic couplings of local and resonance modes. The simple model under consideration in the present work involves only even powers of longitudinal displacements $u_\parallel$ and implies the limit $\omega_\parallel \ll \Omega_\perp$, which enables these relations to get simplified:

$$\Delta \equiv \Omega_{max} - \Omega_0 = \Delta_0 + \Delta_1 \tag{8}$$

$$\Delta_0 = \frac{\hbar}{m^2 \Omega_0 \omega_\parallel} \widetilde{\Phi}_4^\parallel(0) \left[n(\omega_\parallel) + \frac{1}{2} \right] \tag{9}$$

$$\binom{\Delta_1}{\Gamma_1} = \frac{\hbar^2}{m^4 \Omega_0 \omega_\parallel^2} n(\omega_\parallel) \left[n(\omega_\parallel) + 1 \right] \frac{1}{N} \sum_{\mathbf{k}} \frac{\left| \widetilde{\Phi}_4^\parallel(\mathbf{k}) \right|^2}{\Omega_{\mathbf{k}} \left[(\Omega_0 - \Omega_{\mathbf{k}})^2 + \eta^2 \right]} \binom{\Omega_0 - \Omega_{\mathbf{k}}}{\eta} \tag{10}$$

where η is the full resonance width of the longitudinal mode,

$$n(\omega) = \left[\exp(\hbar\omega / k_B T) - 1 \right]^{-1} \tag{11}$$

is the temperature-dependent factor of the Bose-Einstein statistics, and

$$\widetilde{\Phi}_4^\parallel(\mathbf{k}) = \Phi_4^\parallel - \frac{9\Phi_3 \Phi_3^\parallel}{m(4\Omega_{\mathbf{k}}^2 - \Omega_0^2)} + \frac{2(\Phi_3^\parallel)^2}{m\Omega_0^2} \tag{12}$$

is the effective value of the coefficient of the quartic anharmonicity renormalized by the cubic anharmonic coefficients. With contributions from the cubic anharmonicity neglected, Eq. (10) are reduced to Eqs. (47) and (48) of Ref. [5]. One can readily see that the renormalized coefficient $\widetilde{\Phi}_4^\parallel(\mathbf{k})$ with k=0 which specifies the spectral shift calculated in the second-order perturbation theory (see Eq. (9)) coincides with the analogous one in Ref. [10] and vanishes if the coefficients specified by Eq. (5) in the central-force model are substituted into it. On the other hand, the spectral line shift and halfwidth calculated in the fourth-order perturbation theory depend on the value of $\widetilde{\Phi}_4^\parallel(\mathbf{k})$ at k≠0:

$$\widetilde{\Phi}_4^\parallel(\mathbf{k}) = 6 \frac{\Phi_3}{l_0} \frac{\Omega_{\mathbf{k}}^2 - \Omega_0^2}{4\Omega_{\mathbf{k}}^2 - \Omega_0^2} \approx 4 \frac{\Phi_3}{l_0} \frac{\Omega_{\mathbf{k}} - \Omega_0}{\Omega_0} \tag{13}$$

and prove to be nonzero.

To estimate Δ_1 and Γ_1, let us express, as in Ref. [11], the coefficient Φ_3 in terms of the bond energy $\mathring{A}_0$ of a Morse potential approximating the function $U(r)$ and introduce the parameter $\Delta\Omega_{band} = \max|\Omega_k - \Omega_0|$ characterizing the width of the local vibration band. Then

$$\begin{pmatrix} \Delta_1 \\ \Gamma_1 \end{pmatrix} \approx 4B\, \frac{\hbar\Omega_0}{E_0}\, \frac{\Omega_0\eta}{\omega_{\parallel}^2}\, n(\omega_{\parallel})\big[n(\omega_{\parallel})+1\big] \begin{pmatrix} (\Delta\Omega_{band}/\eta)^3 \\ (\Delta\Omega_{band}/\eta)^2 \end{pmatrix} \tag{14}$$

where $B = \hbar/2ml_0^2$ is the rotation constant of the light atom with the mass m residing at the distance l_0 from the corresponding heavy atom of the surface. For a hydrogen atom and $l_0 \approx 1$ Å, we obtain $B \approx 19$ cm^{-1}. The ratio $\hbar\Omega_0/E_0$ for H on the Si(111) [14] and C(111) [15,16] surfaces as well as that for H in hydroxyl groups on various oxide surfaces [17] is about 0.1. On the other hand, the ratio $\Omega_0\eta/\omega_{\parallel}^2$ for the same systems changes in a wide range, from 0.2 to 2.5. Then at $k_B T = \hbar\omega_{\parallel}$ and $\Delta\Omega_{band} = \eta$, we arrive at $\Delta_1 \approx \Gamma_1 \approx 1 - 10$ cm^{-1}.

Clearly the band effect concerned proves to be rather slight for systems with weak lateral interactions, which can be exemplified by the system H/C(111): $\Delta\Omega_{band} \approx 14$ cm^{-1}, $\eta \approx 120$ cm^{-1} [16], and the full width is found as $2\Gamma_1 \approx 0.04$ cm^{-1}. However, another system, OH/SiO$_2$, presents the case where the low-frequency mode corresponds to the rotational vibration of a hydroxyl group around the Si-O bond with the frequency $\omega_{\parallel} \approx 100$ cm^{-1}; this vibration is slightly coupled with the phonon spectrum of the substrate and hence the value $\eta \approx 4$ cm^{-1} turns out to be small enough and comparable to $\Delta\Omega_{band} \approx 2$ cm^{-1} [14]. In this case, relation (13) gives the value $2\Gamma_1 \approx 4$ cm^{-1} of the same order of magnitude as experimentally observed ones [18]. The 2x1 phase of CO/NaCl(100) is another example of a system characterized by $\eta \approx 2,8$ cm^{-1}, and $\Delta\Omega_{band} \approx 6$ cm^{-1} (judging by the scale of the Davydov splitting for the spectral line of CO local vibrations which is observed at temperatures T < 25 K) [3,4].

Thus, in parallel with other dephasing mechanisms, the band dephasing effect can notably contribute to the shift and width of the spectral line of local vibrations, provided the band width for these local vibrations is compared to the resonance width of the low-frequency mode. The model involving the potential of central forces permitted the "pure" band effect to be treated: the spectral line shift and width are proportional to the cubed and the squared band width for local vibrations, $\Delta\Omega_{band}$, and vanish at $\Delta\Omega_{band} = 0$.

Acknowledgments

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