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SHIFT AND BROADENING OF ADSORBATE VIBRATIONAL MODES

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The shift and broadening of the vibrational frequency of the adsorbate on a metal surface are calculated on the basis of two different models. The first model is an anharmonic one which includes multiphonon processes to all order in first-order perturbation theory. We show that anharmonic damping due to multiphonon processes is substantial for CO adsorbed on a Ni(100) surface and small for H adsorbed on a W(100) surface. At room temperature multiphonon processes with $n > 2$ are very important even in cases when the frequency of vibration of the adsorbate lies below twice the maximum phonon frequency of the substrate (n is the order of the process). For the C–Ni stretching mode of top-bonded CO on Ni(100) our results are in accord with the experimental data. The second model is an electronic one which includes the electron–hole pair loss mechanism. We show that the observed shift and broadening of the C–O stretching vibration mode for a CO molecule adsorbed on Cu(100) and for a H atom adsorbed on a W(100) surface can be explained on the basis of this model. Variation of the shift and broadening of the CO stretching mode with the distance from a CO molecule to Ni(111) surface are calculated.

1. Introduction

Molecular vibrations at surfaces form an increasingly active area of research [1]. From such studies one can obtain information about adsorbed species, adsorption sites, electronic rearrangements, nature of chemisorption bond and possible reaction path. The prime experimental tools are infrared reflection adsorption spectroscopies (IRS) and high resolution electron energy loss spectroscopy (EELS). Among the most interesting phenomena associated with the vibrational states of chemisorbed molecules is the change in vibrational frequencies and lifetime of a molecule upon adsorption. There are various mechanisms which give rise to the shift and broadening of the vibrational state of chemisorbed molecule on metal surface:

(a) *Inhomogeneous shift and broadening.* This shift and broadening must be due to the interaction between the adsorbed molecules either directly through the dipole fields of the vibrating molecules or by an indirect interaction mediated by the metal. The best studied (theoretically and experimentally) inhomogeneous systems are isotopic mixtures and incomplete monolayers where the dipole–dipole interaction gives rise to asymmetric, broadened adsorption peaks, which usually shifted towards higher frequencies [2].

(b) *Vibrational phase relaxation.* This mechanism is due to fluctuations of the vibrational frequency due to anharmonic coupling to surrounding modes. Pure dephasing processes generally dominate condensed phase homogeneous linewidths, particularly at high temperatures, but at surface the problem is not so clear [3].

(c) *Vibrational shift and broadening.* This mechanism is associated with the hybridization of the vibrational modes of chemisorbed molecule and the phonon modes of the metal. The effectiveness of this mechanism depends not only on the anharmonicity of the potential well but also on the magnitude of ω_0/ω_c, where ω_0 is the frequency of the adsorbate vibrational mode, ω_c is the highest phonon frequency of the metal. For H on W(100) $\omega_0/\omega_c \approx 4$, for the C–O stretching vibration of CO on Cu(100) $\omega_0/\omega_c \approx 9$. Thus one should expect damping, due to emission of phonons, to be rather unimportant for this vibrational modes. However, for the C–Ni stretching vibration of CO on the Ni(100) surface $\omega_0/\omega_c \approx 2$ so that damping due to emission of phonons could be expected to be an important damping mechanism. The anharmonic lifetime broadening was calculated by Braun and Pashitskii [4] for the case of zero substrate temperature and by Ariyasu et al. [5] who reported calculations of two-phonon contribution to the anharmonic linewidth. In a recent paper Persson [3d] claims that for the Ni–CO stretching vibration for CO on Ni(100) three-phonon processes are negligible and only two-phonon processes play an important role. However, Persson used the Debye model which does not describes properly the properties of the phonon density of states of an atom in a clean nickel surface.

(d) *Shift and broadening due to emission of electron–hole pairs.* If an adparticle is dipole active, the electromagnetic field of the vibration dipole penetrates into the metal and results in creation of electron–hole pairs. This damping mechanism the so-called Landau damping was considered in a number of works [6]. However, as it was shown by Persson and Persson [7], if an admolecule is close to the surface the more effective mechanism of electron–hole creation is associated with fluctuation of the electron level position of the admolecule during vibration (Anderson damping mechanism). If there is an adsorbate induced resonance state close to the Fermi energy ϵ_F, then as the molecule is vibrating, this resonance state will move up and down in energy around ϵ_F. The periodic filling and emptying of the resonance state $|a\rangle$ during the vibration of the adsorbate molecule will lead to non-adiabatic processes. Within the frame of the level fluctuation model (LFM) the shift and broadening of adsorbate vibrational modes were qualitatively considered by Mal'shukov [8a] and Ueba [8b]. Persson and Persson [7] calculated the lifetime broadening for the C–O stretching vibration of CO on Cu(100) and found an excellent agreement with the experimental findings. There is a transition from the quasi-adiabatic limit $\Delta \gg \omega_0$ to the strong non-adiabatic limit $\Delta \ll \omega_0$ when the admolecule is moved from the surface. (Δ is the half width of the electron resonance state of the adsorbate.) Formulas for lifetime broadening and shift describing this transition were derived by Volokitin [9].

The article proceeds as follows. In section 2 the lifetime broadening due to anharmonicity of the interaction potential is considered. We obtain an expression for the damping rate which includes all the important multiphonon terms to the first-order perturbation theory. Explicit results for magnitude and temperature variation of vibrational lifetime broadening are given for H on W(100) and for top-bonded CO on Ni(100).

In section 3, a generalization of the LFM is considered. We take into account the fluctuations of the position of the electron level of adsorbate during vibration as well as its halfwidth Δ.

2. Phonon mechanism of lifetime broadening

In describing the anharmonic damping of the localized vibrational mode of the adsorbate it is convenient to use a zero-order Hamiltonian which adequately describes the motion of the adsorbed particle under the influence of the average potential of the substrate. The thermal fluctuations of the interaction potential around the average value induce transitions between the states of the oscillator. The total Hamiltonian,

$$H = H_\ell + H_p + H_i, \tag{1}$$

is the sum of the lattice Hamiltonian H_ℓ, particle Hamiltonian H_p, and interaction Hamiltonian H_i [10]

$$H_\ell = \sum_\lambda \hbar\omega_\lambda b_\lambda^+ b_\lambda, \tag{2}$$

$$H_p = p^2/2\mu + \langle V(Q, z)\rangle, \tag{3}$$

$$H_i = V(Q, z) - \langle V(Q, z)\rangle. \tag{4}$$

where λ labels to phonons, ω_λ is the phonon frequency, b_λ^+ and b_λ are the corresponding creation and annihilation operators, p is the momentum of the adsorbed particle, μ is the reduced mass of the lattice atom– adsorbed particle pair, the thermal average of the lattice–particle interaction over an equilibrium phonon distribution is given by

$$\langle V(Q, z)\rangle = \mathrm{Sp}_\ell[\rho_\ell V(Q, z)], \tag{5}$$

$$\rho_\ell = \exp(-\beta H_\ell)/z_\ell, \tag{6}$$

$$z_\ell = \mathrm{Sp}_\ell[\exp(-\beta H_\ell)]. \tag{7}$$

$\beta = (k_\mathrm{B}T)^{-1}$, T is the lattice temperature and k_B is Boltzmann's constant. We confine ourselves to a model in which the adsorbed particle moves in a direction perpendicular to the surface, binds to a lattice atom and interacts with it through a Morse potential. One can easily consider a bridge binding and include the interaction with more lattice atoms. The Morse interaction between the adsorbed particle and the surface atom is

$$V(Q, z) = D\{\exp[-2\alpha(z - Q_0 - u - r_0)] - 2\exp[-\alpha(z - Q_0 - u - r_0)]\}. \tag{8}$$

Here z is the position of the adsorbed particle and $Q = Q_0 + u$ is the position of the surface atom (Q_0 is the equilibrium position and u is the displacement away from it). The thermal average $\langle V(Q, z)\rangle$ is given by [10].

$$\langle V(Q, z)\rangle = D'\{\exp[-2\alpha(z - Q_0 - r_0')] - 2\exp[-\alpha(z - Q_0 - r_0')]\}, \tag{9}$$

$$D' = D\exp[-\alpha^2\langle u^2\rangle], \tag{10}$$

$$r_0' - r_0 = (3\alpha/2)\langle u^2\rangle. \tag{11}$$

Note that the average potential can be written as a Morse potential with new values D' and r_0' for parameters D and r_0. The bound state eigenvalues for the Morse oscillator are given by [10]

$$E_n = -(\hbar^2\alpha^2/2\mu)(k - n - \tfrac{1}{2})^2,$$

where n is an integer confined to the interval $0 \leqslant n \leqslant k - \frac{1}{2}$, $k = (2\mu D')^{1/2}/\hbar\alpha$. For $D \gg \hbar\omega_0$, where $\hbar\omega_0 = E_1 - E_0$, the parameter α may be calculated from formula $\alpha^2 = \mu\omega_0^2/2D'$. When the Morse oscillator is in the first excited state $|1\rangle$ then in a semiclassical picture the interaction Hamiltonian H_i can be written in the time-dependent form [6a]

$$V_\mathrm{sc}(t) = V_{01}\,\mathrm{e}^{-\mathrm{i}\omega_0 t} + V_{10}\,\mathrm{e}^{\mathrm{i}\omega_0 t}, \tag{12}$$

$$V_{01} = \langle 0|H_\mathrm{i}|1\rangle = V_{10}$$

The lifetime τ is determined by [6a]

$$\overline{\mathrm{d}\epsilon/\mathrm{d}t} = \epsilon_0/\tau, \tag{13}$$

where $\epsilon_0 = \hbar\omega_0$ and $\overline{\mathrm{d}\epsilon/\mathrm{d}t}$ is the time-averaged flow of energy into the substrate due to interaction of the excited atom with the phonon system. Accordingly to the linear response theory [11]:

$$\overline{\mathrm{d}\epsilon/\mathrm{d}t} = 2\omega_0\alpha''(\omega_0), \tag{14}$$

where the imaginary part of the generalized susceptibility is given by [11]

$$\alpha''(\omega_0) = \frac{1}{2\hbar[1+n(\omega_0)]}\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega_0 t}\,\langle V_{01}(t)V_{10}(0)\rangle\,\mathrm{d}t, \tag{15}$$

$$V_{01}(t) = \mathrm{e}^{\mathrm{i}H_{\ell}t/\hbar}\,V_{01}\,\mathrm{e}^{-\mathrm{i}H_{\ell}t/\hbar},$$

$$n(\omega_0) = \left[\exp(\hbar\omega_0/k_{\mathrm{B}}T) - 1\right]^{-1}.$$

Comparing (14) and (13) we obtain

$$\Gamma = \hbar/\tau = \frac{1}{\hbar[1+n(\omega_0)]}\int_{-\infty}^{\infty} C_{01}(t)\,\mathrm{e}^{\mathrm{i}\omega_0 t}\,\mathrm{d}t, \tag{16}$$

$$C_{01}(t) = \langle V_{01}(t)V_{10}(0)\rangle.$$

The correlation function $C_{mn}(t)$ was calculated by Efrima et al. [10]. Using the results of this work we obtain

$$\begin{aligned} C_{01}(t) = D'^2\big\{ & B^2\left[\exp(4\alpha^2\langle u(t)u\rangle) - 1\right] + 4A^2\left[\exp(\alpha^2\langle u(t)u\rangle) - 1\right] \\ & -4AB\left[\exp(2\alpha^2\langle u(t)u\rangle) - 1\right]\big\}, \end{aligned} \tag{17}$$

$$A = (1/2k)(2k-3)^{1/2}, \quad B = A(2k-1)/k.$$

Within the harmonic approximation the correlation function $\langle u(t)u\rangle$ is given by [10]

$$\langle u(t)u\rangle = \frac{\hbar}{2M}\int_0^{\omega_c}\frac{\rho(\omega)}{\omega}\left[\mathrm{ctgh}\left(\frac{\hbar\omega\beta}{2}\right)\cos(\omega t) - \mathrm{i}\,\sin(\omega t)\right]\mathrm{d}\omega, \tag{18}$$

where M is the mass of the lattice adatom, $\rho(\omega)$ is a local density of vibrational states for a surface atom of the substrate.

Since $\langle u(t)u\rangle$ is exponentiated in eq. (17) the linewidth expression Γ includes multiphonon processes to all orders. The one-phonon, two-phonon, three-phonon, ... contributions to the linewidth can be recovered through a power series expansion of $C_{01}(t)$ in $\langle u(t)u\rangle$.

The evaluation of the linewidth requires knowledge of the local density of vibrational states $\rho(\omega)$. For a Debye model $\rho(\omega)$ is equal to

$$\rho(\omega) = \begin{cases} \dfrac{3\omega^2}{\omega_{\mathrm{D}}^3}, & \omega \leqslant \omega_c, \\ 0, & \omega > \omega_c. \end{cases} \tag{19}$$

For this model in limiting cases we obtain the following analytical expressions

$$\Gamma=\frac{2\pi D'^2}{\hbar\omega_0}\left(\frac{2k-3}{k^2}\right)\sum_{j=j_{\min}}^{\infty}\sum_{s=0}^{\infty}\sum_{l=0}^{j}(-1)^{l+j}\left[\frac{2k-1}{k}2^{j+s}-2\right]^2$$
$$\times\left[\frac{3}{4}\frac{\mu}{M}\frac{\hbar\omega_0}{D'}\left(\frac{\omega_0}{\omega_c}\right)^3\right]^{j+s}\left(\frac{j\omega_c-\omega_0}{\omega_0}\right)^{2j+2s-l-j}\left(\frac{\omega_c}{\omega_0}\right)^{l}$$
$$\times\frac{1}{(2j+2s-l-1)!}\,\frac{1}{(j-l)!s!l!},\qquad(20)$$

if $T=0$, and

$$\Gamma=\frac{2\pi D'^2}{\hbar\omega_0}\,\frac{1}{[1+n(\omega_0)]}\left(\frac{2k-3}{4k^2}\right)\sum_{j=j_{\min}}^{\infty}\sum_{s=0}^{\infty}(-1)^{s}\left[\frac{2k-1}{k}2^{j+2s}-2\right]^2$$
$$\times\left[\frac{3}{4}\frac{\mu}{M}\left(\frac{\omega_0}{\omega_c}\right)^3\frac{k_BT}{D'}\right]^{j+2s}\left(\frac{j\omega_c-\omega_0}{\omega_0}\right)^{j+2s-1}\frac{1}{(j+2s-1)!s!(j+s)!},\qquad(21)$$

if $k_BT \gg \hbar\omega_c$. Integer $j_{\min}$ is determined by the condition $(j_{\min}-1)\omega_c < \omega_0 < j_{\min}\omega_c$, $j_{\min}$ is equal to a minimum number of substrate phonons which must be created in order to induce the transition $|1\rangle \to |0\rangle$. The Debye model is useful for a qualitative analysis. For example, for the perpendicular vibration of hydrogen on the W(100) surface $\omega_0 = 3.7\omega_c = 0.13$ eV, $D = 3$ eV [4]. Using this value it is easy to see that the anharmonic lifetime broadening for the vibration of H on W(100) is very large even at high temperature. For example, at $T = 10^3$ K lifetime broadening $\tau = \hbar/\Gamma \approx 10^{-7}$ s. For a quantitative calculation it is necessarily to use a more realistic model for $\rho(\omega)$. The spectral density $\rho_{zz}(\omega)$ for vertical motion of a Ni atom in the clean (111) surface was calculated by Black [12] using a continued fraction approach. This function is shown in fig. 1. We propose that for the (100) surface the spectral density $\rho_{zz}(\omega)$ has the same form. Using this spectral density we calculated the

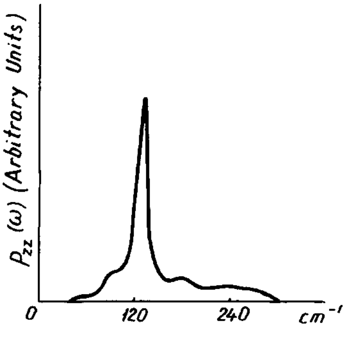

Fig. 1. Spectral density $\rho_{zz}(\omega)$ for vertical motion of a atom in the clean (111) surface (ref. [12]).

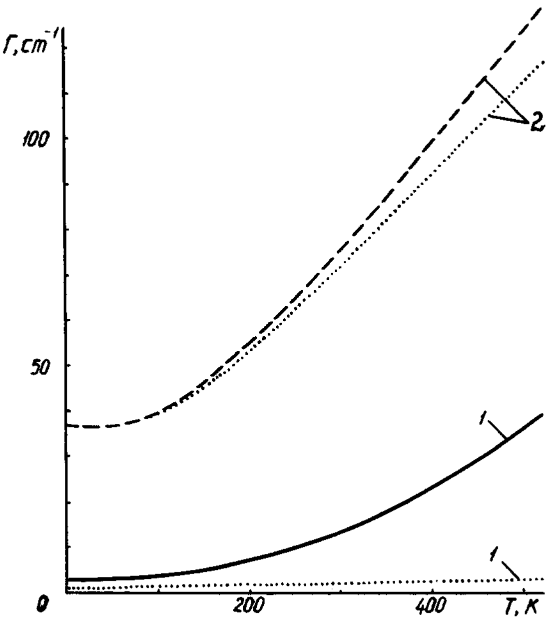

Fig. 2. Temperature variation of the linewidth for the Ni–CO vibration for CO/Ni(100). (1) Spectral density $\rho_{zz}(\omega)$ from ref. [12] was used in the calculation. (2) Debye model was used. The dotted curve is contribution from two-phonon processes only.

linewidth of the perpendicular vibration of the stretching vibration for CO top bonded to a Ni atom on the Ni(100) surface. For this case $\omega_0 = 480\ \mathrm{cm}^{-1}$ and $D = 1.0 \times 10^4\ \mathrm{cm}^{-1}$ [5a]. At room temperature the calculated linewidth of the C–Ni vibrational mode for CO adsorbed on Ni(100) is 13.3 cm^{-1}, a value pleasingly close to the 15 cm^{-1} linewidth reported by Chiang et al. [13]. Fig. 2 shows the temperature dependence of the linewidth and also the contribution to the linewidth from two-phonon processes only. In the case which we considered the vibration frequency of the adsorbate lies below twice the maximum phonon frequency of the substrate ($\omega_c = 300\ \mathrm{cm}^{-1}$), when the transition $|1\rangle \rightarrow |0\rangle$ requires two phonons as minimum. As a rule for each additional phonon needed the relaxation rate is reduced by a factor of ≈ 1.5–2 orders [14]. Thus one might expect that the multiphonon processes with $n > 2$ (n is the order of the phonon process) would be negligible. However, this is not so for the Ni–CO vibration for CO/Ni(100). The Ni(100) surface spectral density $\rho_{zz}(\omega)$ has a sharp maximum at $\omega \approx \omega_p \approx 150\ \mathrm{cm}^{-1}$. Thus the phonon states with $\omega \approx \omega_p$ give the main contribution to the calculated linewidth. For this states $\omega_0/\omega_p \approx 3$ and thus three-phonon processes are also important. For comparison in fig. 2 we show the temperature dependence of the linewidth calculated for a Debye model. For a Debye model the difference between the two-phonon and multiphonon linewidth is small. Therefore the conclusion made by Persson [3d], about the negligible role of three-phonon processes is an artifact. The two-phonon contribution to the anharmonic linewidth was calculated by Ariyasu et al. [5] who found a good agreement with the observed linewidth for the Ni–CO vibration for CO/Ni(100). However, formula (2.11) in their paper [5b] contains a wrong factor four. Note also that the formula for the linewidth obtained by Persson [3d] is wrong by lacking a factor $[1+n(\omega_0)]^{-1}$.

3. Electronic mechanism of shift and lifetime broadening

The model Hamiltonian in the LFM is described by [4,7–9]

$$H = H_e + H_{ph} + H_{e-ph}, \tag{22}$$

$$H_e = \sum_{\sigma} \epsilon_a n_{a\sigma} + \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{k\sigma} \left(V_{ak} C^+_{a\sigma} C_{k\sigma} + \text{h.c.} \right) + U n_{a\sigma} n_{a-\sigma}, \tag{23}$$

$$H_{ph} = \hbar\omega_0 B^+ B, \tag{24}$$

$$H_{e-ph} = \lambda_0 (b^+ + b) F, \tag{25}$$

$$F = \sum_{k\sigma} \left[\epsilon'_a n_{a\sigma} + V'_{ak} \left(C^+_{a\sigma} C_{k\sigma} + \text{h.c.} \right) \right], \tag{26}$$

$\lambda_0 = (\hbar/2M\omega_0)^{1/2}$, $\epsilon'_a = \mathrm{d}\epsilon_a/\mathrm{d}q$, $V'_{ak} = \mathrm{d}V_{ak}/\mathrm{d}q$, q is the displacement of the oscillator away from the equilibrium position, $n_a = C^+_{a\sigma} C_{a\sigma}$, $n_k = C^+_{k\sigma} C_{k\sigma}$, $C^+_{a\sigma}$ ($C_{a\sigma}$) and $C^+_{k\sigma}$ ($C_{k\sigma}$) are fermion creation (destruction) operators of electrons with spin σ in the molecular state $|a\rangle$ with energy ϵ_a and metal state $|k\rangle$ with energy ϵ_k, V_{ak} is the adparticle–metal coupling, U is the Coulomb interaction between electrons of opposite spins at the adparticle. Let us first consider the case when $V'_{ak} = 0$ and $U = 0$. In this case we may omit the symbol σ. The Fourier transformation of the phonon Green function

$$D(\omega) = -\mathrm{i} \int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t}\, D(t)\, \mathrm{d}t,$$

$$D(t) = \langle \mathrm{T}\, \varphi(t)\, \varphi(0) \rangle, \quad \varphi(t) = b^+(t) + b(t)$$

is given by [8,9]

$$D(\omega) = \frac{2\omega_0}{\omega^2 - \omega_0^2 - 2\omega_0 \lambda^2 \Pi(\omega)}, \tag{27}$$

where in the second-order pertubation theory on $\lambda = \lambda_0 \epsilon'_a$ the polarization operator $\Pi(\omega)$ is given by

$$\Pi(\omega) = \int_{-\infty}^{\epsilon_F} \mathrm{d}\epsilon \int_{\epsilon_F}^{\infty} \mathrm{d}\epsilon'\, \rho_a(\epsilon)\, \rho_a(\epsilon') \left\{ \frac{1}{\omega - \epsilon' + \epsilon} - \frac{1}{\omega + \epsilon' - \epsilon} \right\}, \tag{28}$$

$$\rho_a(\epsilon) = \frac{1}{\pi} \frac{\Delta}{(\epsilon - \epsilon_a)^2 + \Delta^2}.$$

In the case when the electron halfwidth Δ is independent of the energy the integral (28) may be evaluated analytically. The result has the form

$$\Pi(\omega - \mathrm{i}\delta) = \Pi'(\omega) + \mathrm{i}\Pi''(\omega), \tag{29}$$

$$\Pi'(\omega) = \frac{\Delta}{\omega^2 + 4\Delta^2}\left\{\frac{2\Delta}{\omega}\left[n_\mathrm{a}(\epsilon_\mathrm{a} + \omega) - n_\mathrm{a}(\epsilon_\mathrm{a} - \omega)\right] + \frac{1}{2\pi}\ln\left[\frac{\rho_\mathrm{a}^2(\epsilon_\mathrm{F})}{\rho_\mathrm{a}(\epsilon_\mathrm{F} + \omega)\,\rho_\mathrm{a}(\epsilon_\mathrm{F} - \omega)}\right]\right\}, \tag{30}$$

$$\Pi''(\omega) = \frac{\Delta}{\omega^2 + 4\Delta^2}\left\{\frac{\Delta}{\pi\omega}\ln\left[\frac{\rho_\mathrm{a}^2(\epsilon_\mathrm{F})}{\rho_\mathrm{a}(\epsilon_\mathrm{F} + \omega)\,\rho_\mathrm{a}(\epsilon_\mathrm{F} - \omega)}\right] + n_\mathrm{a}(\epsilon_\mathrm{a} - \omega) - n_\mathrm{a}(\epsilon_\mathrm{a} + \omega)\right\}, \tag{31}$$

$$n_\mathrm{a}(\epsilon) = \frac{1}{\pi}\operatorname{ctg}^{-1}\left(\frac{\epsilon - \epsilon_\mathrm{F}}{\Delta}\right). \tag{32}$$

The linewidth and shift of the vibrational mode are determined by

$$\Delta\omega = \lambda^2\Pi'(\omega_0), \tag{33}$$

$$\Gamma = 2\lambda^2\Pi''(\omega_0). \tag{34}$$

From the formulas (33) and (34) we obtain that in the quasi-adiabatic limit ($\Delta \gg \omega_0$) $\Gamma \approx \Delta^{-2}$, $\Delta\omega \approx \Delta^{-1}$ if $|\epsilon_\mathrm{a} - \epsilon_\mathrm{F}| \ll \Delta$. In opposite limit ($\Delta \ll \omega_0$) $\Gamma \approx \Delta$, $\Delta\omega \approx \Delta^2$. When the molecule moves from the surface, Δ monotonically decreases [15], thus we have a transition from the quasi-adiabatic limit $\Delta \gg \omega_0$ to the strong non-adiabatic limit $\Delta \ll \omega_0$. For small distances from the adsorbate to the surface Γ changes faster than $\Delta\omega$, on the long distance the reverse is true. The dependence of the lifetime broadening Γ and frequency shift $\Delta\omega$ on the distance d from the surface are given in fig. 3. The parameters were choosen to describe the C–O stretching vibrational mode for CO adsorbed on the Ni(111). We take an exponential form for the $2\pi^*$ antibonding resonance for CO/Ni(111) [4,15]

$$\Delta = \Delta_0 \exp[-2\gamma(d - d_0)], \tag{35}$$

where $\gamma = (2m_\mathrm{e}\phi/\hbar^2)^{1/2}$, $\phi = 5.10$ eV is the work function for nickel [16], $\Delta_0 = 2.75$ eV [17], $\omega_0 = 2056\ \mathrm{cm}^{-1}$ [18], $|\epsilon_\mathrm{a}'| = 11$ eV/Å [19], $\epsilon_\mathrm{a}(d_0) - \epsilon_\mathrm{F} = 3$ eV [18]. There is a dramatic increase in the damping rate and shift of vibrational frequency when the molecule moves away from the surface and an adsorbate resonance crosses the Fermi level. Such an enhancement of the damping rate was discussed earlier by Persson and Hellsing [20] using another approach.

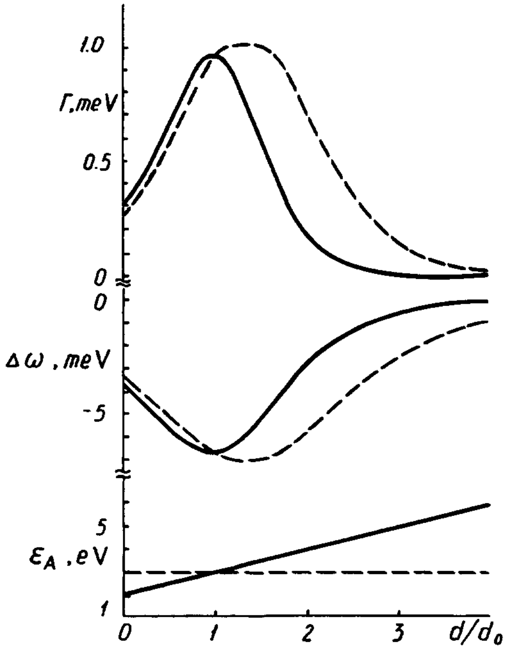

Fig. 3. (a) Linewidth Γ, (b) frequency shift $\Delta\omega$, (c) electron level position ϵ_a for the C–O stretching vibration for CO adsorbed on the Ni(111) as a function of the distance d from the surface ($\epsilon_F = 0$). The solid curves $\epsilon_a(d) = \text{constant}$. The dashed curves $\epsilon_a(d) = \epsilon_a(d_0) + \alpha(d/d_0 - 1)$, $\alpha = 1$ eV, $2\gamma d_0 = 1$.

When the admolecule is removed from the surface, splitting of the vibrational spectra may occur. Let us consider the equation for the self-frequencies.

$$\omega^2 - \omega_0^2 - 2\omega_0\lambda^2\Pi'(\omega) = 0. \tag{36}$$

It is convenient to investigate this equation graphically. For this purpose we rewrite it in a dimensionless form

$$\frac{y - y_0}{\nu} = -\frac{\Pi'(y)}{\Pi'(0)}, \tag{37}$$

where $y = (\omega/\Delta)^2$, $y_0 = (\omega_0/\Delta)^2$,

$$\nu = -2\omega_0(\lambda_0\epsilon_a')^2\Pi'(0)/\Delta^2 = 2\omega_0\left(\frac{\epsilon_a'\lambda_0}{\Delta}\right)^2\rho_a(\epsilon_F).$$

The graphical solution of eq. (37) is shown in fig. 4. When the admolecule is removed from the surface, then $\Delta \to 0$, $\nu \to \infty$ and the angle between the straight line and the horizontal axis decreases. Therefore at different distances for the admolecule from the surface there are possible situations where eq. (37)

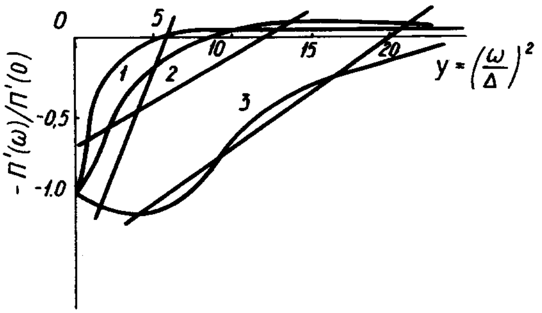

Fig. 4. Graphical solution of the eq. (4): (1) $\epsilon_a = \epsilon_F$; (2) $\epsilon_a - \epsilon_F = 1$; (3) $\epsilon_a - \epsilon_F = 2.5$. All energy are given in units of the electron halfwidth Δ.

has one, two or three solutions. At $\Delta \to 0$ eq. (37) always has two solutions: one at $\omega \approx \omega_0$ and the second at $\omega \approx \Delta$, if $\epsilon_a - \epsilon_F = 0$. The line shape of a vibrational line in the presence of electron–hole decay processes as measured by a charge-coupled probe is given by the imaginary part of a generalized susceptibility function [21].

$$\alpha(\omega) = -\mu_D^2 D(\omega + i\delta), \tag{38}$$

where μ_D has been termed the dynamic dipole of the adsorbed molecule. The peaks of $\alpha(\omega)$ are determined by the roots of eq. (37). The function $\Pi''(\omega)$ is plotted in fig. 5. The function $\Pi''(\omega)$ strongly depends on ω in the region $\omega \approx \Delta$.

In the quasi-adiabatic limit $\Delta \gg \omega_0$ the formula for the lifetime broadening and the shift are significantly simplified and have the form

$$\Gamma = 2\pi\hbar\omega_0 [\lambda\rho_a(\epsilon_F)]^2, \tag{39}$$

$$\Delta\omega = -\lambda^2\rho_a(\epsilon_F). \tag{40}$$

Formulas (39) and (40) were firstly derived by Mal'shukov [8a]. Using the relation $\delta n = \lambda\rho_a(\epsilon_F)$ where δn is the fluctuation in the number of electrons in the orbital $|a\rangle$ during one vibration, formulas (39) and (40) may be rewritten in the form

$$\Gamma = 2\pi\hbar\omega_0(\delta n)^2, \tag{41}$$

$$\Delta\omega = -\lambda\delta n, \tag{42}$$

For CO on Cu(100) $\delta n = 0.03$ [7], $\omega_0 = 0.26$ eV, $|\epsilon_a'| = 11$ eV/Å [19], $\lambda_0 = (\hbar/2M\omega_0)^{1/2} = 0.033$ Å. Taking into account the orbital and spin degeneracy of the $2\pi^*$ affinity level of CO, Persson and Persson obtained [7] $\tau_{\text{theory}} = \hbar/\Gamma = 1.8 \times 10^{-12}$ s, which is in fair agreement with the experimental

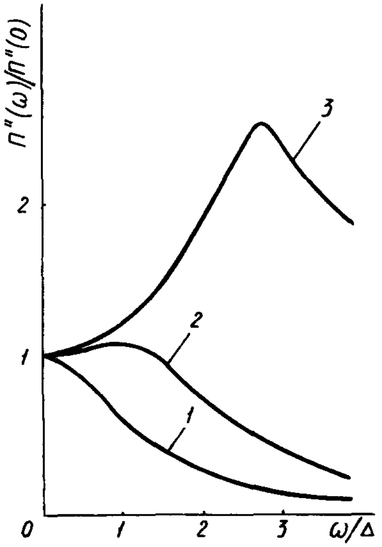

Fig. 5. Imaginary part of the polarization operator $\Pi''(\omega)$ as a function of ω. Notations are the same as in fig. 4.

findings $\tau_{\text{exp}} = 3 \times 10^{-12}$ s [22]. From formula (42) we obtain $\Delta\omega_{\text{e}} = -88$ cm^{-1}. The total shift

$$\Delta\omega_{\text{tot}} = \Delta\omega_{\text{e}} + \Delta\omega_{\text{ph}} + \Delta\omega_{\text{im}},$$

where $\Delta\omega_{\text{im}} = -2$ cm^{-1} [6d] is the shift due to the image forces, $\Delta\omega_{\text{ph}} = 33 \pm 6$ cm^{-1} [23] is the shift due to coupling of the C–O and C–Cu stretching vibration. Thus we obtain $\Delta\omega_{\text{tot}} = -57 \pm 6$ cm^{-1} which is remarkably close to the experimental shift $\Delta\omega_{\text{exp}} = -60 \pm 10$ cm^{-1} [22].

Let us now consider the case when $V_{ak} \neq 0$ and $U \neq 0$. Using formula (15) with $H_{\text{e-ph}}$ from (25) as a perturbation we obtain the following expression for the linewidth

$$\Gamma = \frac{1}{M\omega_0[1 + n(\omega_0)]} \operatorname{Re}\left[\int_0^\infty e^{i\omega_0 t} \langle F(t) F(0) \rangle \, dt\right], \tag{43}$$

This formula may be compared with the expression for the friction coefficient [24]

$$\eta = \beta M^{-1} \operatorname{Re}\left[\int_0^\infty \langle \tilde{F}(t)\ \tilde{F} \rangle \, dt\right], \tag{44}$$

$$\tilde{F} = F - \langle F \rangle.$$

Comparing eq. (43) and (44) one can deduce the relation

$$\lim_{\omega_0 \to 0} \lim_{T \to 0} \Gamma = \lim_{T \to 0} \hbar\eta. \tag{45}$$

Thus in a quasi-adiabatic limit and at $T = 0$ K, Γ and $\hbar\eta$ are equal to each other. Using the results obtained for the friction coefficient [25] and relation (45) we obtain at $T = 0$ K.

$$\Gamma_0(\epsilon_F) = \frac{4\hbar^2}{\pi M}\left\{\sin^2\delta(\epsilon_F)\left[\frac{\langle|V'_{ak}|^2\rangle_{\epsilon_F}}{\langle|V_{ak}|^2\rangle_{\epsilon_F}} - \left(\frac{\Delta'}{2\Delta}\right)^2\right] + \tfrac{1}{2}[\delta'(\epsilon_F)]^2\right\}, \tag{46}$$

where $\langle|V'_{ak}|^2\rangle_{\epsilon_F}$ $(\langle|V_{ak}|^2\rangle_{\epsilon_F})$ is the average of $|V'_{ak}|^2$ $(|V_{ak}|^2)$ over k on the energy contour $\epsilon = \epsilon_F$, $\delta(\epsilon_F)$ is the phase shift at $\epsilon = \epsilon_F$ which even for the case $U \neq 0$ is given by [26]

$$\delta(\epsilon_F) = \mathrm{tg}^{-1}[\Delta/(\epsilon_a - \epsilon_F)]. \tag{47}$$

Note that the role of the Coulomb interaction U between electron of opposite spin occupying the adatom valence level is negligible at $T = 0$ K because of in this case expression (46) for the linewidth has the same form for interacting ($U \neq 0$) and independent ($U = 0$) electrons.

It may be shown [25] that the first (second) term in eq. (46) is negligible for vibrations normal (parallel) to the surface:

$$\Gamma_{0\parallel} = \frac{4\hbar^2}{\pi M}\sin^2\delta\frac{\langle|V'_{ak}|^2\rangle_{\epsilon_F}}{\langle|V_{ak}|^2\rangle_{\epsilon_F}}, \tag{48}$$

$$\Gamma_{0\perp} = \frac{2\hbar^2}{\pi M}(\delta')^2. \tag{49}$$

If the surface is flat, we have [25a]

$$\Gamma_\parallel \simeq \frac{8}{5\pi}\frac{m_e}{M}\epsilon_F\sin^2\delta, \tag{50}$$

where m_e is the electron mass. The electron energy level ϵ_a varies with the distance d, accordingly [27]

$$\epsilon_a = \epsilon_a^0 + \varphi = -I + \frac{e^2}{4(d - d_{im})}, \tag{51}$$

where $d = d_0 + q$ is the distance to the surface, d_0 is the equilibrium position of the adatom and q is the displacement away from it, d_{im} is the position of the image plane, φ is the image potential, I is the ionization potential. For hydrogen chemisorption $\varphi \simeq 3.4$ eV [28]. From eq. (51) we obtain $|\epsilon'_a| = |\varphi'| = 4\varphi^2/e^2 = 3.4$ eV/Å. For the 1s level linewidth we take an exponential form (35), then $\Delta' = -2\gamma\Delta$, $\Delta = 2$ eV [4] for hydrogen chemisorption on W(100). Thus taking $\epsilon_F \simeq 5$ eV from (48) and (49) we obtain $\Gamma_\perp = 2.6$ meV and $\Gamma_\parallel = 0.2$ meV. For vibration normal to the surface theoretical linewidth is close to the experimental one $\Gamma_{exp} = 1.7$ meV [29].

For $\omega_0 \gg k_B T_K$, where T_K is the Kondo temperature, we do not expect a strong temperature dependence of Γ. For independent electrons from formula (43) for $\Delta \gg \omega_0$ we obtain

$$\begin{aligned}\Gamma(T) &= \frac{1}{\omega_0} \int_{-\infty}^{\infty} \frac{\Gamma_0(\epsilon)\, f(\epsilon)\, [1 - f(\epsilon + \omega_0)]\, \mathrm{d}\epsilon}{[1 + n(\omega_0)]} \\ &= \frac{1}{\omega_0} \int_{-\infty}^{\infty} \Gamma_0(\epsilon)\, [f(\epsilon) - f(\epsilon + \omega_0)]\, \mathrm{d}\epsilon \simeq -\int_{-\infty}^{\infty} \Gamma_0(\epsilon) \frac{\partial f}{\partial \epsilon}\, \mathrm{d}\epsilon \\ &\simeq \Gamma_0(\epsilon_F) + \frac{\pi^2}{6} \frac{\partial^2 \Gamma_0(\epsilon)}{\partial^2 \epsilon}\bigg|_{\epsilon = \epsilon_F} (k_B T)^2 = \Gamma_0(\epsilon_F) \left\{ 1 + O\left[\left(\frac{k_B T}{\Delta} \right)^2 \right] \right\}, \qquad (52)\end{aligned}$$

where $f(\epsilon)$ is the Fermi distribution function, $\Gamma_0(\epsilon)$ is given by (46) with ϵ instead of ϵ_F. Thus as long as $k_B T \ll \Delta$ the temperature dependence of the linewidth associated with the electron–hole pairs loss mechanism is negligible.

4. Conclusion

In the present work we have calculated the linewidth and shift of the vibrational modes of the adsorbate on the metal surface using two different model. The first model is an anharmonic one which includes multiphonon processes to all order in first-order perturbation theory. Using this model we show that the anharmonic damping can give an important contribution to the linewidth of adsorbate vibrational mode if $\omega_0 < 2\omega_c$. The second model is an electronic one which includes the electron–hole pairs loss mechanism. Using the Anderson–Newns type model we show that the observed linewidth and shift of the C–O stretching vibrational mode for a CO molecule adsorbed on the Cu(100) surface can be explained in terms of excitation of the electron–hole pairs in the metal due to oscillation of charge between the CO $2\pi^*$ orbital and the metal during vibration. For a hydrogen atom adsorbed on W(100) the estimated linewidth is also close to the experimental one. One may differentiate between damping provided by electron–hole excitations and anharmonicity through the temperature variation of the linewidth. When $\omega_0 \gg k_B T$, the width due to damping into electron–hole pairs is nearly independent of T. The width due to multiphonon processes is strongly temperature dependent. At room temperature the multiphonon processes with $n > 2$ give a very important contribution even in the case when $\omega_0 < 2\omega_c$, where n is the order of the processes.

Let us now give a short discussion of the lifetime for H on W(100). For this system the dynamical charge e^* is equal to 0.04 [30]. Using the relation

$$\delta n = e^* \lambda_0 / (d - d_{\mathrm{im}})$$

Braun et al. [4] made an estimate $\delta n \approx 0.01$. Putting this value and $\omega_0 = 0.13$ eV into formula (41) we obtain $\Gamma \approx 0.1$ eV which is about 10 times smaller than the observed one ($\Gamma_{\text{exp}} = 1.7$ eV). The discrepancy between this estimate and experiment for H/W the system is connected with the screening of the adatom charge by the conduction electrons. For the C–O stretching vibration for adsorbed on Cu(100) the problem of screening in the absence of electron overlap was solved by Persson and Ryberg [31]. It was shown that if this screening is taken into account one obtains a greater dynamical dipole moment and thus greater δn. For a hydrogen chemisorption the problem of screening is more difficult because of large charge overlap of the hydrogen atom with the metal. We obtain the right value for Γ if we put in eq. (38) $\delta n \approx 0.06$.

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