THE INFLUENCE OF LATERAL INTERACTIONS ON THE VIBRATIONAL SPECTRUM OF ADSORBED CO

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Vibrational spectroscopy of adsorbed CO often reveals strong shifts of the CO stretch absorption band to higher frequencies as a function of increasing coverage. It is shown that such shifts are due essentially to dipole–dipole interactions. The extent of the experimentally observed effect can, however, only be reproduced when screening by the substrate is taken into account properly.

1. Introduction

The spectra of vibrational modes [1] of adsorbed CO show an absorption band at a frequency similar to that of the gas phase C–O stretching mode ($2143 \ cm^{-1}$. $265.7 \ meV$). If is often observed that the maximum of the band shifts to higher energies by $25–130 \ cm^{-1}$ ($3–16 \ meV$) on increasing the coverage [2–5] although in one case a shift in the other direction has been observed as well [6]. A number of explanations have been proposed for this effect [7–10]. Just recently Mahan and Lucas [8] have re-examined the theory of vibrations in adsorbed CO layers which had originally been proposed by Hammaker, Francis and Eischens [7]. Whereas Hammaker et al. treated only the direct dipole–dipole interactions of different excited molecules, Mahan and Lucas also considered the image charge screening by the metal substrate; the interactions of a dipole with other dipoles and their respective images was treated exactly, but the interaction with its own image dipole was not properly included. Moskovits and Hulse [9] on the other hand estimated the change of the electric field in the adsorbate layer by a complex dielectric function, but did not consider the screening by the metal electrons which will change the dielectric behaviour of the adlayer markedly. These three previous models could only explain 30–40% of the observed shift and the authors therefore concluded that the experimentally observed shift was due mainly to other mechanisms. In this paper it is shown that, as long as the adsorption site does not change, the observed

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shifts can be accounted for fully by dipole—dipole interactions, when the screening by the metal conduction electrons is properly considered.

The theory is based on a microscopic description of the electrodynamic field in the adlayer. For the CO polarizability gas phase values are used. Further parameters are the distance between the induced molecular dipole and the reference plane for the image effect, the damping of the dipole which manifests itself in the line width, and the frequency ω_0 of the normal mode associated with the C—O stretch vibration of a single adsorbed CO molecule without screening by the metal electrons.

Whereas in angular-resolved photoemission studies it has been found that the coverage dependence of adsorbate-induced emission peaks is essentially due to the overlap of wavefunctions on neighbouring adsorbates [11,12] the results of this paper show that in studying vibrations the influence of overlap appears to be negligible.

2. Theory

In this section the theory is briefly described bearing in mind that the vibrations are excited by a long wavelength electric field as in IR reflection absorption spectroscopy. Due to the strong screening effect by the metal electrons the macroscopic electric field and the induced microscopic dipole moments in the CO molecules are oriented perpendicular to the surface [13]. Thus only the normal components are considered in the following. The induced oscillating dipole moments are proportional to the local electric field, the total dipole moment of the adsorbed particle is thus given by:

$$p(R_j, \omega, t) = p_{st} + \alpha(\omega) E^{local}(R_j, \omega, t) , \qquad (1)$$

where p_{st} is the static dipole moment of a single adsorbed particle without the screening by the metal conduction electrons. $\alpha(\omega)$ is the polarizability which is a microscopic, molecular property. For axial molecules such as CO it is different for an electric field parallel and perpendicular to the axis, $\alpha_{\parallel}(\omega)$ is usually greater than $\alpha_{\perp}(\omega)$. $E^{local}(R_j, \omega, t)$ is the microscopic electric field at the dipole at the adsorption site R_j without the field of the dipole itself. For an *isolated* layer the local field is the sum of the incident macroscopic field

$$E^0(r, \omega, t) = E^0 \exp[i(\omega t - k \cdot r)] , \quad \text{with } k = 2\pi/\lambda ,$$

and the field $E_j^{other\ dipoles}$ due to the dipoles of the neighbouring molecules. The far (radiation) field $(r \gg \lambda)$ of all oscillating dipoles at the illuminated side of the layer gives the reflected field and that at the non-illuminated side gives together with $E^0(r, \omega, t)$ the transmitted field. For an *adsorbed* layer these two terms together with the field of the dipole itself at R_j interact with the metal electrons, yielding a change in the local field and therefore a change in the induced dipole

moments. The interaction of the incident field (normal component) can be described by a reflectivity of the metal which in the far field will reach the value r_p of Fresnel's formula for p-polarized light. The interaction of the dipoles is accounted for in terms of the classical concept of fictitious image dipoles:

$$E_j^{local} = \widetilde{E}_j^0 + E_j^{other\,dipoles} + E_j^{own\,image} + E_j^{other\,images} . \tag{2}$$

The indices refer to the site R_j at which the fields act. $\widetilde{E}_j^0$ is the incident field plus the field reflected by the metal surface. The dipoles are approximated by point dipoles. In this first step, the calculation of the local field in the adlayer, the larger contributions come from the near zone ($r \ll \lambda$) of the dipoles. The different contributions to the field E_j^{local} are therefore:

$$E_j^{own\,image} = p_j/4d^3 , \tag{3}$$

$$E_j^{other\,dipoles} = - \sum_{\substack{k \\ k \neq j}} p_k/(|R_j - R_k|^3) , \tag{4}$$

$$E_j^{other\,images} = - \sum_{\substack{k \\ k \neq j}} p_k/(|R_j - R_k|^2 + 4d^2)^{3/2} + 12 p_k d^2/(|R_j - R_k|^2 + 4d^2)^{5/2} . \tag{5}$$

For a periodic array of dipoles, eq. (5) leads to:

$$E_j^{other\,images} = -2\pi pn \sum_g g \exp(-2dg) + p/4d^3 . \tag{6}$$

The summations run over all occupied adsorption sites R_k excluding R_j. Here d is the distance between the effective surface of the metal and the dipole. This is the most important but also a somewhat uncertain parameter of the theory because the position of the surface plane of the metal is not well-defined due to the "tailing" of the metal electrons into the vacuum. Further the effect of imperfect screening of a charge distribution close to the surface tends to reduce the effect of the image and this can be described by an appropriate position of the image plane. Appelbaum and Hamann [14] and Zaremba and Kohn [15] have calculated this position of the reference plane within a jellium model. If a is the separation between the substrate layers parallel to the surface, the position of the reference plane should be at $a/2 + Z_0$ in front of the first substrate layer, with Z_0 about 0.2 (for $d = 1$ Å and the electron density parameter r_s about 2) [14,15]. In this sense the classical formula for the image effect is a reasonable first approximation. It should be noted that the effect of imperfect screening is included in the position of the reference plane: Close to the surface, Z_0 decreases strongly with decreasing adsorbate–substrate distance which reduces the classical effect. In a more exact treatment the delay in the response of the metal conduction electrons to the dipole could be considered but this would give only negligible changes because the metal is an excellent conductor

at these frequencies (e.g., for Pt at the frequency 2200 cm^{-1}, $\epsilon = -120 + 340i$ [1]). In the sum over other image dipoles it is assumed that the field parallel to the surface cancels at the site of the diret dipoles [16], thus in IR only dipoles perpendicular to the surface can be excited. Eq. (6) [17] is only valid for ordered adsorption; g are the two-dimensional reciprocal lattice vectors of the adlayer and n is the density of adsorbed CO molecules. The wavelength of the light is long compared to atomic distances and the microscopic dipole moments will therefore be almost completely in phase. Combining eqs. (1)–(5) yields:

$$p(R_j, \omega, t) = \frac{p_{st}}{1 + \alpha(\omega)[S(\theta) - 1/4d^3]} + \frac{\alpha(\omega)\,\tilde{E}^0(R_j, \omega, t)}{1 + \alpha(\omega)[S(\theta) - 1/4d^3]}, \tag{7}$$

with

$$S(\theta) = \sum_{\substack{k \\ k \neq j}} \frac{1}{|R_k - R_j|^3} + \frac{1}{(|R_k - R_j|^2 + 4d^2)^{3/2}} - \frac{12d^2}{(|R_k - R_j|^2 + 4d^2)^{5/2}}. \tag{8}$$

In eq. (8) the propagation time and the phase difference of the field from the surrounding dipoles is neglected because the wavelength is very large compared to the diameter of the area in which the sums have to be evaluated. The first term of eq. (7) describes the change of the static dipole moment and thus the change of the work function [11]. The second term has the same time dependence as the incident field:

$$p(R_j, \omega, t) - \frac{p_{st}}{1 + \alpha(\omega)[S(\theta) - 1/4d^3]} = p(\omega) \exp[i(\omega t - k \cdot R_j)]. \tag{9}$$

The electrodynamic field reflected by an adsorbate covered surface, measured in an IR absorption reflection experiment, is the superposition of the field directly reflected by the metal plus the far field of the oscillating dipoles and their image dipoles. The change in the reflected intensity due to the adlayer is then given by:

$$\begin{aligned} \Delta R &\sim \langle [\text{Re}(r_p E^0 + E^{\text{dipoles}} + E^{\text{images}})]^2 \rangle - \langle [\text{Re}(r_p E^0)]^2 \rangle \\ &= 2\langle \text{Re}(r_p E^0(\omega, t))\,\text{Re}(E^{\text{dipoles}}(\omega, t) + E^{\text{images}}(\omega, t)) \rangle \\ &\quad + \langle [\text{Re}(E^{\text{dipoles}}(\omega, t) + E^{\text{images}}(\omega, t))]^2 \rangle. \end{aligned} \tag{10}$$

The pointed brackets indicate the time average. $r_p E^0$ is the field directly reflected by the metal. The field of the dipoles and of the image dipoles in the far field is given by the interfering fields

$$- \frac{\ddot{p}(R_j, \omega, t - |r - R_j|/c)}{c^2 |r - R_j|} + \frac{[\ddot{p}(R_j, \omega, t - |r - R_j|/c)(r - R_j)](r - R_j)}{c^2 |r - R_j|^3}$$

of the different oscillators. Because the first term in (10) is dominant, the change in

the reflected intensity is

$$\Delta R \sim n\omega^2 [\text{Re}(p(\omega)) \, \text{Re}(r_\text{p}) - \text{Im}(p(\omega)) \, \text{Im}(r_\text{p})] \; . \tag{11}$$

At near to grazing incidence (usually $87°$ to the surface normal) the real part of the reflection coefficient of the metal vanishes (e.g. for Pt at $87°$, 2200 cm^{-1} $r_\text{p} = (0, 0.52)$). The change of the reflected intensity, eq. (11), is then proportional to the imaginary part of the dipole moment $p(\omega)$.

It is assumed that the polarizability $\alpha(\omega)$ can be written as a sum of an electronic part, describing induced dipoles due to the electronic polarization, and a part caused by the vibrations of the atom cores. The electronic part is assumed to be independent of frequency in the frequency range of interest and the vibrational part is assumed to have a single Lorentzian line shape:

$$\alpha(\omega) = \alpha_\text{e} + \frac{\alpha_\text{v}}{1 - (\omega/\omega_0)^2 + i\gamma(\omega/\omega_0)} \; . \tag{12}$$

ω_0 is the vibration frequency of the normal mode associated with the C–O stretch. $\gamma\omega_0$ is the line width. ω_0 is expected to be a little lower than the gas phase stretching frequency because the C–O bond is weakened due to the fact that the antibonding $2\pi^*$ orbital is partly filled in the adsorbed molecule [10]. (This shift to lower frequencies often appears to be larger than the upward shift due to the coupling of the C–O mode with the lower frequency metal–CO mode.) ω_0 is related to the zero coverage limit of the vibration frequency: from equation (7) and (12) it follows with $S(\theta) = 0$ and negligible damping that the dipole moment has the maximum at [20]

$$\omega^\text{zero cov.} = \omega_0 [1 - \alpha_\text{v}/(4d^3 - \alpha_\text{e})]^{1/2} \; . \tag{13}$$

The electric field of the dipole's own image lowers the vibrational frequency of the single adsorbed CO molecule by the order of 50 cm^{-1}; this shift increases with increasing the electronic polarizability α_e and with decreasing d. The experimentally observed decrease of the frequency upon chemisorption of a single CO molecule is partly due to this effect. Eq. (7) shows that the induced dipole moment depends on the difference $S(\theta) - 1/4d^3$, because $S(\theta)$ for a full adlayer has roughly the same magnitude as the self image term $1/4d^3$ both these effects tend to cancel each other or S becomes even bigger than $1/4d^3$ with increasing coverage. It is therefore expected that the observed shift on increasing coverage will be of the same magnitude as the self image shift of a single adsorbed molecule. For the free molecule experimental results yield the total polarizabilities $\alpha_\parallel^\text{gas} = 2.6 \text{ Å}^3$, $\alpha_\perp^\text{gas} = 1.63 \text{ Å}^3$ [13] and the vibrational part is $\alpha_\text{v}^\text{gas} = 0.057 \text{ Å}^3$ [1,8]. The electronic part α_e is the difference between the total polarizability and the vibrational part. ω_0 in particular depends on the C–O bond as well as on the chemisorption bond: it will increase if the C–O bond strength or the metal–CO bond strength increase. It will thus be different for different substrates and for different adsorption sites. The evaluations

given below are therefore limited to a coverage range where only one kind of adsorption site is occupied, providing one fixed ω_0.

3. Results and discussion

Eq. (7) shows that the response of a polarizable particle close to a metal surface to a field $(\tilde{E}^0)$ is different from that of the particle in vacuum. This can be described by introducing an effective polarizability

$$\alpha^*(\omega, \theta) = \alpha(\omega)\{1 + \alpha(\omega)[S(\theta) - 1/(4d^3)]\}^{-1} . \tag{14}$$

The free particle polarizability $\alpha(\omega)$ is thus changed by the coverage and frequency dependent factor

$$\{1 + \alpha(\omega)[S(\theta) - 1/(4d^3)]\}^{-1} .$$

Mahan and Lucas neglected the $1/4d^3$ term in eq. (14) and thus the important enhancement of the polarisability α^* at small coverage. Further they used the average value for the free molecular static polarizability $\alpha_{av} = 1.95$ Å^3 wheras for CO standing perpendicular to the surface the bigger value $\alpha_\| = 2.6$ Å^3 is the appropriate choice. Due to these two points Mahan and Lucas were unable to reproduce the experimental observed shifts. A further results of their neglect of the $1/4d^3$ term in eq. (14) is that their model becomes nearly independent on the effect of imperfect screening, which is not the fact in our treatment. It should be noted that only as long as we use the interpretation given by the self-consistent jellium model [14,15] our theory works well; a Fermi–Thomas screening mechanism [21,8] appears to be not sufficient, it would reduce the extent of the calculated shifts essentially.

In fig. 1 the calculated change in the reflected intensity (the second term of eq. (11)) for CO/Pd(100) is shown for coverages up to $\Theta = 0.5$ and are compared to the experimental results [4]. At $\theta = 0.5$ an ordered c(4 × 2)R45° structure is formed with CO molecules in bridging positions. The IR spectra of Bradshaw and Hoffmann [4] indicate that bridging positions are also occupied in the range of disordered adsorption $0 < \theta < 0.5$. From fitting the experimental results we determine the parameters of our theory: $\omega_0 = 1950$ cm^{-1}, the distance between dipole and image reference plane $d = 0.96$ Å, and the line width $\gamma\omega_0 = 10$ cm^{-1}. With these values the stretch frequency of a single adsorbed CO molecule is lowered by 56 cm^{-1} due only to the interaction with its own image dipole. Because d is the distance between the induced dipole moment and the effective image plane, we estimate the distance between the center of the first Pd layer and the carbon atom of about 1.6 Å which is a quite reasonable value. It should be noted that the values for ω_0 and for γ are not sensitive to the magnitude of the shift but only to the absolute frequency positions and to the width of the peaks respectively. For $\theta = 0.5$ the value $S = 0.24$ Å^3 is calculated from eq. (8). Different coverages ($0 \leqslant \theta \leqslant 0.5$) are simulated by setting $S(\theta) = F(\theta)S(0.5)$ with $0 \leqslant F(\theta) \leqslant 1$. The limits $F = 0$ and $F = 1$ correspond to the coverages $\theta = 0$ and $\theta = 0.5$. The correspondence between F
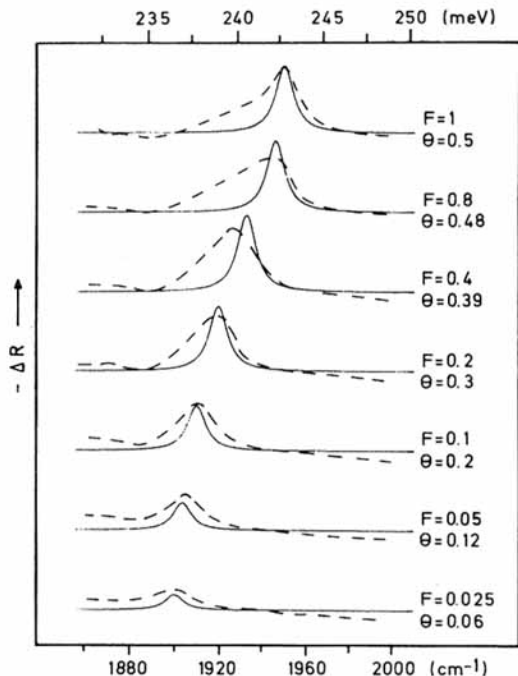
Fig. 1. Calculated change of the reflected intensity $(-\Delta R)$ (arbitrary units) due to the adlayer for the system CO/Pd(100) for several coverages (full line, $F = 0.025-1$) and experimental IR reflection absorption spectra (dashed line, $\theta = 0.06-0.5$) [4].

and Θ inbetween these two limits is doubtful because such spectra should de deter-mined by the ensemble of different arrangements of neighbours which will also give rise to the observed broadening of the peaks in this coverage region. The shift between zero and half monolayer coverage is in good agreement with the experi-mental results. On top of this marked shift due to the dipole—dipole interaction there may also be superimposed a shift in the same direction due to the coverage-dependent interaction of the metal electrons with the $2\pi^*$ orbital [10]. However, as this latter effect appears to be associated with a decrease in binding energy in the CO/Pd(100) system, then a shift in the opposite direction is expected due to the reduced coupling of the CO molecule to the surface. Both effects would enter the theory by a coverage dependence of ω_0. The first contribution is not known nu-merically but the second contribution can be estimated within a purely mechanical model and this would give a downward shift of the C—O stretch frequency by about $10 \, \text{cm}^{-1}$. Due to the agreement obtained in fig. 1 it would not seem unrea-sonable that these two additional effects may be roughly of the same magnitude and therefore cancel, implying that ω_0 can be treated as independent of coverage.

For another system, CO/Pt(111), Shigeishi and King [3] and more recently

Krebs and Lüth [22] have measured a shift of the CO stretching mode between zero coverage and half coverage of 35 and 32 cm^{-1} respectively. The latter authors have shown that there are two different adsorption sites and that the observed shift could be in part due to a change in the bonding to the substrate. Nevertheless we tentatively also applied our theory to this system. With an adjusted distance $d =$ 1.03 Å we calculated a shift of 32 cm^{-1} which shows that the experimentally observed shift could be due purely to a dipole–dipole coupling mechanism.

4. Conclusion

A theory of IR absorption reflection spectroscopy is described. The main parameter is the distance between the induced dipole moment and the effective image plane. The shift of the absorption band of the C–O stretch vibration with increasing coverage is calculated for the systems CO/Pd(100) and CO/Pt(111). The results are in good agreement with the experimental data. Contrary to previous investigations we conclude that the shift can be totally explained by a dipole–dipole coupling mechanism.

Acknowledgements

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