Microscopic treatment of the IR spectroscopy of CO physisorbed on NaCl(100)

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The infrared spectrum of a monolayer of CO physisorbed on the NaCl(100) surface has been calculated using the discrete dipole approach. The corresponding description is rigorously microscopic and accounts exactly for the occurring local fields in both the substrate and the adsorbed monolayer. The model does not impose restrictions upon the configuration and links smoothly the microscopy of the system to the externally observable macroscopic response. Using established values for the geometry and polarizabilities of the NaCl, we have calculated the integrated absorbance of the system. We find that, in order to arrive at an agreement between theory and experiment, the usual values for the polarizability and/or the height above the surface of the CO molecule should be decreased. No unique answer as to the value of these two parameters can be obtained from interpreting IR absorption experiments.

1. Introduction

The infrared absorption of simple molecules like CO and CO₂ adsorbed onto alkali halide surfaces has recently obtained much attention, both by experimentalists and theoreticians, since it is believed to be a model system for physisorption. I.e., one presumes that the bonding is dominated by classical electrostatic forces and the properties of adsorbed species remain close to their gas phase value. After the pioneering work of e.g. Gevitzman [1], Heidberg [2] and Zecchina [3], the group of Richardson and Ewing [4] has extensively studied the adsorption of CO onto NaCl. They tried to explain their experimental results by applying the thin film continuum theory of McIntyre and Aspnes [5]. Chen and Schaich [6] compared three microscopic models based on the *d*-parameter formalism namely: a continuum–continuum model where both overlayer and substrate are described as a dielectric continuum, a discrete–continuum approach where the CO is described as a layer of point polarizable dipoles, and a discrete–discrete model. However, none of these models appears to be able to describe the experi-

ments property as their results for the integrated absorbance show a deviation of at least 30%. Richardson and Ewing, Chen and Schaich as well as Zecchina attribute this discrepancy to the fact that for the vibrational polarizability of CO they use the gas phase value. The change of this value upon adsorption should account for the deviation of 30%.

In order to investigate this problem we developed, within the discrete dipole approach, a model of calculating the optical response of a thick dielectric slab in an exact way [7]. This “thick slab method”, as we will call it, links a real-space description of the surface to a description in reciprocal space (using a normal mode decomposition) of the bulk. This way the optical response of the thick slab can be calculated starting from the microscopic Maxwell equations, with a limited number of parameters, while retaining the surface sensitivity of the method developed in ref. [8], which is only suited for thin slabs. An analogous method for semi-infinite crystals has been described in ref. [9]. The advantage of this approach over continuum descriptions or hybrid approaches as the one described by Chen and Schaich [6,10] is

that the relation between the microscopy of the system and the macroscopic observable phenomena (absorbance, reflectance) is very straightforward.

2. Method of calculation

A description of the theory can be found in ref. [7]. The parallel translational symmetry reduces the number of dipole strengths to be calculated in each layer to one, the representing dipole of the layer. The method links 2 surface slabs, whose representing dipoles are described in real space, to a bulk slab, whose dipole strengths are calculated using a normal mode decomposition:

$$\mathbf{p}_{\text{Br},V} = \sum_{m=1}^M \nu_m \mathbf{u}_{mv} \exp(iq_m a \gamma V), \quad (1)$$

where v indexes the N_B representing dipoles of the bulk cell, which is the repeating unit in the bulk cell in all 3 spatial dimensions, V indexes the N bulk cells in the direction perpendicular to the surface (there are N of those), M is the number of normal modes, ν_m the strength of the normal modes, $\mathbf{u}_{mv}$ the normal mode vectors, q_m the normal mode wave vectors and γ the height of a bulk cell in units of the bulk lattice parameter a . The addition of the two surface slabs, containing the CO overlayer and a number of NaCl cells of bulk geometry, allows for the restriction of the number of normal modes in the bulk slab to 4. The values q_m and $\mathbf{u}_m$ are obtained by finding the eigenvalues and eigenvectors of a secular equation, which is the discrete analogue of the Fresnel equation of continuum theories [7]. Upon solution of the representing dipoles $\mathbf{p}_i$ of the surface slabs and the normal mode strengths ν_m of the bulk, the reflection and transmission coefficient can be obtained straightforwardly as:

$$r = \left(\frac{ik^2}{2\epsilon_0 \beta k_z a^2} \right) \left(\frac{\mathbf{E}_0 \cdot \mathbf{P}(\underline{k})}{|\mathbf{E}_0|} \right), \quad (2a)$$

$$t = 1 + \left(\frac{ik^2}{2\epsilon_0 \beta k_z a^2} \right) \left(\frac{\mathbf{E}_0 \cdot \mathbf{P}(\underline{k})}{|\mathbf{E}_0|} \right), \quad (2b)$$

with:

$$\begin{aligned} \mathbf{P}(\underline{k}) &= \sum_{j=1}^{N_s} e^{-ik_z r_j} \mathbf{p}_j, \\ e^{-ik_z d_s} \sum_{m=1}^4 \left[\sum_{w=1}^{N_B} e^{-i(k_z - q_m)z_w^B} \right. \\ &\quad \times \left. \left(\frac{1 - e^{-i(k_z - q_m)\gamma d_B}}{1 - e^{-i(k_z - q_m)d_B}} \right) \right] \nu_m \mathbf{u}_m, \end{aligned} \quad (3)$$

where $\mathbf{r}_j$ is the position vector of the j th surface dipole, z_w^B the z -coordinate of the w th bulk dipole with respect to the origin of the first bulk cell, d_s the thickness of the first surface cell, d_B the thickness of the bulk cell and βa^2 the area of the two-dimensional surface unit cell. $\underline{k} = (k_{\parallel}, k_z)$ is the wavevector of the incident light and $\underline{k} = (k_{\parallel}, -k_z)$.

3. Calculations and results

We specify the configuration as follows. In the bulk slab each dipole represents one NaCl pair at the Cl^- location, having polarizability $\alpha(\text{NaCl}) = 3.24 \text{ \AA}^3$ [12]. In the surface slabs each Na^+ or Cl^- ion corresponds to a separate dipole. For the polarizability of the Na^+ ion the theoretical value $\alpha(\text{Na}^+) = 0.16 \text{ \AA}^3$ has been taken from ref. [12]. The polarizability of the Cl^- ion makes up for the remainder yielding $\alpha(\text{Cl}^-) = 3.08 \text{ \AA}^3$. All layers are (100) oriented.

The CO molecules are adsorbed on top of the Na^+ ions [4] at a height of d and the polarizability-tensor of a CO molecule will be given by $\hat{\alpha}(\text{CO}) = \hat{\alpha}_e + \hat{\alpha}_v$, where $\hat{\alpha}_e$ is the electronic polarizability tensor which has the following non-zero components [13]:

$$\alpha_{xx}^e = \alpha_{yy}^e = 1.79 \text{ \AA}^3, \quad \alpha_{zz}^e = 2.32 \text{ \AA}^3.$$

$\hat{\alpha}_v$ is the vibrational polarizability tensor which contains only zeros except:

$$\alpha_{zz}^v = \alpha_v [1 - (\omega^2 + i\omega\gamma)/\bar{\omega}^2]^{-1},$$

with $\alpha_v = 0.053 \text{ \AA}^3$, taken from gas phase data [14]. $\gamma = 0.42 \text{ cm}^{-1}$, $\bar{\omega} = 2148.99 \text{ cm}^{-1}$, have been

chosen such as to reproduce location and broadening of the resonance at 55 K [4].

With these parameters we calculate the absorbance for p-polarized light, of two NaCl-slabs, each of them covered on both sides by a CO monolayer. The two slabs are oriented as described in ref. [4], so that the angle of incidence for both slabs is 60° . The absorbance is calculated by means of the equation [7]:

$$A_p = 2 \log_{10}(T_0/T), \quad (4)$$

where T_0 is the transmittance of a 3 mm thick NaCl slab without CO-overlayers and T of one with CO-overlayers. The integrated absorbance:

$$\tilde{A}_p = \int_{-\infty}^{+\infty} A_p(E) dE, \quad (5)$$

is calculated numerically over a large enough energy interval. Taking $d = 3.3 \text{ \AA}$ as in ref. [6], we find $\tilde{A}_p = 0.024 \text{ cm}^{-1}$ (see fig. 1). The experimentally measured value equals 0.019 cm^{-1} [4], 19% below the theoretical value.

This discrepancy between experimental and theoretical result could have a number of causes. First of all, the vibrational motion of the NaCl (surface phonons) could account for part of the difference, but its frequency appears to be much smaller than that of the CO vibration, so this effect can be ruled out. Further, the static electric field produced by the NaCl lattice creates a change

Fig. 1. The absorption spectrum of 2 NaCl slabs, covered on both sides by a CO monolayer for p-polarized light incident under an angle of 60° . The distance from the monolayer to its substrate is $3.3 \text{ \AA}$ and for α_v the gas phase value is taken.

Fig. 2. Relation between α_v and d for an integrated absorbance $\tilde{A}_p$ of 0.019 cm^{-1} .

in the vibrational polarizability of CO [15], but this effect is very small ($< 1\%$) and it increases α_v and thus $\tilde{A}_p$. A substantial change in α_v due to quantum effects is also not expected, because of the negligible overlap between the wave functions of CO and its substrate at a distance of $3.3 \text{ \AA}$. So the only way to reduce the theoretically obtained integrated absorbance is to change the distance between CO and the NaCl lattice. Demanding quantitative agreement between the theoretical integrated absorbance and the experimental one, a relation between α_v and d can be obtained which is shown in fig. 2. The gas phase value of α_v turn out to be well beyond the theoretical α_v s over the entire range of plausible d -values. Also we have found that d has to be decreased in order to decrease $\tilde{A}_p$. For a microscopic interpretation of this phenomenon one needs the local absorbance of the i th layer given by [7]:

$$A_i = - \frac{k^2}{\beta k_z \epsilon_0 a^2 |E_0|^2} \text{Im} \left(E_{\text{loc},i}^{*T}(\alpha_i)^{*T} E_{\text{loc},i} \right), \quad (6)$$

the $*$ indicating the complex conjugate and Im meaning: “the imaginary part of”. Using eq. (6) we see that the only two ways to decrease the local absorbance of the CO overlayers are the decreases of the local field at the CO site or of the polarizability of CO, which requires a quantum-mechanical change in this molecule upon adsorption. To study the first effect we give in table 1 the magni-

Table 1

 $E_{\text{dip}}^R = E_{\text{dip}}/E_0$ (E_0 : amplitude incoming beam), at the sites of the dipoles in the first 4 layers of the surface slab

	E_{dip}^R				
	$d = 1.9740 \text{ \AA}$	$d = 2.4252 \text{ \AA}$	$d = 2.8764 \text{ \AA}$	$d = 3.3276 \text{ \AA}$	$d = 3.6660 \text{ \AA}$
CO	12.9359	14.3025	14.9272	15.2854	15.5027
Cl_1^-	5.5444	3.1014	1.7231	0.9823	0.7104
Na_1^+	22.3140	10.0873	4.8454	2.3980	1.4251
Cl_2^-	0.6514	0.5096	0.4619	0.4449	0.4369
Na_2^+	1.3010	0.7794	0.5505	0.4704	0.4563
Cl_3^-	0.4411	0.4387	0.4381	0.4379	0.4373
Na_3^+	0.4468	0.4440	0.4405	0.4392	0.4375

tude of the internal field E_{dip} in the four outermost layers for varying distance between CO and NaCl; E_{dip} is the electric field emitted by the dipoles only. We have used $\alpha_v = 0.047 \text{ \AA}^3$ and $\omega = 2155.09 \text{ cm}^{-1}$, the peak value [4]. It is clear that with decreasing distance the internal field in the CO layer decreases but the internal field at the Cl^- and Na^+ ions rises steeply. Therefore as the internal field of the NaCl-layers does not contribute to the absorbance of the slabs, because $\alpha(\text{Cl}^-)$ nor $\alpha(\text{Na}^+)$ have an imaginary part, the absorbance will decrease with decreasing distance.

Interpreting the result of an IR spectroscopic absorbance measurement, does not give an exclusive answer as to the value of the vibrational polarizability of CO adsorbed on NaCl(100) or its distance to the surface. For, if we use the gas phase value of α_v , we end up with a distance d which is so short that the assumption of virtually unmodified wavefunctions becomes untenable. On the other hand, if we use a value of the distance quoted in literature, we need a drastic change in α_v and there appears to be no mechanism which could, at such a distance, account for this change. We conclude that upon adsorption of CO on the (100) surface of NaCl, the vibrational polarizability of CO will decrease with respect to its gas phase value and its distance to this surface will decrease with respect to the value of about $3.0 \text{ \AA}$, usually quoted in literature [1,6]. This means that the original assumptions of most authors who

studied this system, i.e., that it is a model system of physisorption, cannot be persisted, a view which is sustained by the high value of the heat of adsorption found by Gevitzman et al. [1].

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