ir spectroscopy of CO physisorbed on NaCl(100): Microscopic treatment

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We present a general treatment of the optical response of a monolayer physisorbed on a thick dielectric slab. The description, based on the discrete-dipole approach, is rigorously microscopic and accounts exactly for the occurring local fields in both the substrate and the monolayer. The model links smoothly the microscopy of the system to the externally observable macroscopic response. Within this theory we treat the optical response in the infrared of a monolayer of CO physisorbed on the NaCl(100) surface. Using established values for the geometry and polarizabilities of the NaCl, we calculate the integrated absorbance of the system. We find that, in order to arrive at an agreement between theory and experiment, one can either decrease the distance between the CO monolayer and the NaCl surface with respect to the values usually quoted in literature and/or decrease the vibrational polarizability of CO with respect to its gas-phase value. No unique answer as to the value of these two parameters can be given by just interpreting ir-absorption experiments.

I. INTRODUCTION

We recently developed a theory, starting from the microscopic Maxwell equations and based on the discrete-dipole approximation, to describe the optical response of a thick dielectric slab.¹ Employing a normal-mode decomposition in the bulk of the material, we were able to reproduce classical continuum results and by using a projection technique we could link the regular bulk to the geometrically and electronically freely chosen surface areas. The most attractive aspect of this "double-cell" method is the direct link it offers between the microscopic quantities (geometry, local polarizabilities, internal fields, etc.) and macroscopic observable quantities (reflectance, transmittance, absorbance, etc.). Furthermore, due to the fact that the optical parameters such as the reflection and transmission coefficients are calculated as the far-field solutions of the waves emitted by all the dipoles of the system, problems concerning additional boundary conditions and the linking of a microscopic picture to a macroscopic one using spatial averages^{2,3} are naturally avoided.

In this paper we will employ the freedom this theory leaves us at the surface by applying it to the case of a monolayer adsorbed on a substrate. The only new parameters required for this step are the location of the monolayer atoms relative to the surface, and the polarizability tensor of these atoms. As a case study we take the ir absorption of CO molecules physisorbed on the NaCl(100) surface. Recently this system has obtained much attention, both by experimentalists and theoreticians, since it is believed to be a model system for physisorption. As a model system it should be possible to describe its optical response assuming that the bonding is dominated by classical electrostatic forces and that the properties of the monolayer will remain close to their gas-phase value. We will investigate this. Chen and Schaich⁴ tried to explain the absorption properties of this

system, as measured experimentally by Richardson *et al.*⁵ Using the *d*-parameter formalism⁶ to incorporate the spatial dispersion at the surface, they end up with too high a value of the integrated absorbance. Chen and Schaich impute this (as well as other workers in this field^{5,7}) to the fact that they have used the gas-phase value of the vibrational polarizability of CO. According to their interpretation, this discrepancy would disappear if one calculates this polarizability for adsorbed CO taking into account quantum-mechanical interactions. We compute, using established values for the geometry and polarizabilities of the NaCl, the integrated absorbance. It appears that in order to arrive at an agreement between theory and experiment, apart from decreasing the vibrational polarizability, it is also possible to lower the height above the surface of the CO molecules with respect to the values normally used in literature. This phenomenon is investigated by studying the value of the internal fields involved.

II. OPTICAL RESPONSE OF DIELECTRIC SLABS

In this paper we will apply the theory of the optical response of thick dielectric slabs, as it has been developed in Ref. 1, to the case of a monolayer adsorbed on a transparent substrate. Since the surface layers are treated in real space in our model, it matters little to the formal theory whether we are dealing with one type of dipole in the whole system (as in Ref. 1) or with a monolayer of different composition. In the latter case only the coordinates and the polarizability tensor of the constituents of the monolayer will be modified as compared to the clean surface. (A possible change in the surface reconstruction or in the optical parameters of the substrate upon absorption of the monolayer will not be considered here.) In order to make this article more self-contained, we will repeat here the most important results of Ref. 1. Furthermore, some of the aspects of the theory will be discussed

in more detail. The notational conventions will be the same as in Ref. 1. In particular, for any vector $\mathbf{u}=(u_x, u_y, u_z)$ we define its reflected counterpart $\underline{\mathbf{u}}$ through $\underline{\mathbf{u}}=(u_x, u_y, -u_z)$.

We consider a thick slab consisting of N' dipole lattice planes obeying the same translational symmetry. The dipole sites in plane j will be defined as

$$\begin{aligned}\mathbf{r}_{j,nm} &= \mathbf{r}_j + \mathbf{s}_{nm} \\ &= \mathbf{r}_j + n\mathbf{s}_1 + m\mathbf{s}_2\end{aligned}\quad (1)$$

(where n and m are integers). The vectors $\mathbf{s}_{nm}$ build a lattice, spanned by $\mathbf{s}_1$ and $\mathbf{s}_2$. These vectors can always be written as

$$\mathbf{s}_1 = a(1, 0, 0), \quad (2a)$$

$$\mathbf{s}_2 = a(\alpha, \beta, 0). \quad (2b)$$

In this definition, a is a normalization length which can have any value, but in this paper it will be set equal to the bulk lattice constant. A requirement for the fulfillment of the parallel translational symmetry is that the incoming beam has a simple plane-wave character:

$$\mathbf{E}_{\text{ext}}(\mathbf{r}) = \mathbf{E}_0 \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (3a)$$

$$\mathbf{k} = (\mathbf{k}_{\parallel}, k_z) = (k_x, k_y, k_z), \quad (3b)$$

where ω represents the frequency and $\mathbf{k}$ the wave vector. If c equals the light velocity as usual, the two quantities are linked through $\omega = ck = c|\mathbf{k}|$. Under those assumptions it can be shown that all the dipoles $\mathbf{p}_{j,nm}$ lying in the same lattice plane at $\mathbf{r}_{j,nm}$ can be related to the characteristic dipole $\mathbf{p}_{j,00} = \mathbf{p}_j$ of that plane through the principle of parallel translational symmetry:

$$\mathbf{p}_{j,nm} = e^{i\mathbf{k} \cdot \mathbf{s}_{nm}} \mathbf{p}_{j,00} = e^{i\mathbf{k} \cdot \mathbf{s}_{nm}} \mathbf{p}_j. \quad (4)$$

From here on all dipoles considered will be characteristic ones. The first and last dipole plane [i.e., the one with the smallest (largest) z coordinate], characterized by the dipole $\mathbf{p}_1$ ($\mathbf{p}_{N'}$), will represent the monolayer adsorbed on both sides of the substrate. We obtain, along the lines of thought of Ref. 1, the following interaction equation for the characteristic dipole $\mathbf{p}_i$ located at $\mathbf{r}_i$:

$$\mathbf{p}_i = \tilde{\alpha}_i \mathbf{E}_{\text{loc},i} = \tilde{\alpha}_i \left[\mathbf{E}_{\text{ext}}(\mathbf{r}_i) + \alpha_0^{-1} \sum_{j=1}^{N'} \tilde{\mathbf{f}}_{ij} \mathbf{p}_j \right], \quad (5a)$$

$$\tilde{\mathbf{f}}_{ij} = \tilde{\mathbf{f}}_j(\mathbf{r}_i) = \tilde{\mathbf{f}}(\mathbf{r}_i - \mathbf{r}_j). \quad (5b)$$

Here $\mathbf{E}_{\text{ext}}(\mathbf{r}_i)$ is the incident electromagnetic field at $\mathbf{r}_i$, $\mathbf{E}_{\text{loc},i}$ the local field at $\mathbf{r}_i$, and $\alpha_0 = 4\pi\epsilon_0 a^3$ is a normalization unit for the polarizability. The key component of these equations are the transfer tensors $\tilde{\mathbf{f}}_{ij}$. We consider three types of transfer tensors. If $|z_i - z_j| > z_0$, with z_0 being of the order of magnitude of the bulk lattice constant a , the transfer tensor is the *far-interplanar* type and the following expression will be used for its evaluation:^{8,9}

$$\tilde{\mathbf{f}}_{ij} = \sum_{p,q} \exp[i\mathbf{k}_{pq} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \tilde{\mathbf{d}}_{pq} \quad (z_i > z_j), \quad (6a)$$

$$\tilde{\mathbf{d}}_{pq} = \frac{2\pi i a}{\beta} \frac{(k^2 \mathbb{1} - \mathbf{k}_{pq} \cdot \mathbf{k}_{pq}^T)}{\kappa_{pq}} = \tilde{\mathbf{d}}(\mathbf{k}_{pq}), \quad (6b)$$

$$\mathbf{k}_{pq} = (\mathbf{k}_{pq}^{\parallel}, k_{pqz}) = (\mathbf{k}_{\parallel} + \mathbf{g}_{pq}^{\parallel}, \kappa_{pq}), \quad (6c)$$

$$\kappa_{pq} = (k^2 - |\mathbf{k}_{\parallel} + \mathbf{g}_{pq}^{\parallel}|^2)^{1/2}. \quad (6d)$$

$\mathbf{g}_{pq}^{\parallel} = p\mathbf{g}_1 + q\mathbf{g}_2$ is a surface reciprocal lattice vector. Equations (6) only hold if $(z_i - z_j)$ is positive. If $(z_i - z_j)$ becomes negative, $\tilde{\mathbf{d}}_{pq}$ in (6b) has to be replaced by

$$\underline{\tilde{\mathbf{d}}}_{pq} = \tilde{\mathbf{d}}(\mathbf{k}_{pq}) = \tilde{\mathbf{d}}(\mathbf{k}_{pq}^{\parallel}, -\kappa_{pq}). \quad (7)$$

If $|z_i - z_j| \leq z_0$, then the transfer tensor is either of the *near-interplanar* type (if $\mathbf{r}_i \neq \mathbf{r}_j$) or of the *intraplanar* type (if $\mathbf{r}_i = \mathbf{r}_j$). In the latter case the self-interaction of the representing dipole, which would cause the lattice sum to diverge, is replaced by the Lorentz radiation damping term $\frac{2}{3}ik^3$. This is indicated by the prime in expression (5a). The exact derivation of these types of transfer tensors for general lattices is given in Appendix A.

In principle the set of interaction equations (5) could be solved by using the "thin-slab" method.¹⁰⁻¹² However, if we want to deal with slabs of macroscopic dimensions the number of dipole planes greatly exceeds any computer capacity. So we will proceed as follows. We will subdivide the thick slab into three subslabs: two surface slabs on either side of the thick slab described in real space in a way analogous to the thin-slab method, and one thick intermediate slab described by means of normal modes. The first surface slab (which will be labeled I) contains N_S^{I} dipole layers and has thickness d_S^{I} . The second surface slab (labeled II) contains N_S^{II} dipole layers and has thickness d_S^{II} . The index for the second surface slab continues uninterruptedly from the last index of the first. N_S is the total number of dipole layers in both surface slabs: $N_S = N_S^{\text{I}} + N_S^{\text{II}}$. In order to describe the bulk slab, we first define a bulk unit cell, which is the smallest unit obeying the parallel translational symmetry, which can build up by repetition in the normal direction the interior of the intermediate slab. Each bulk unit cell contains N_B characteristic dipoles, controlling their own bulk plane of dipoles, and has a height of d_B . The bulklike intermediate slab contains N bulk cells and its characteristic dipoles are located at the sites $\mathbf{r}_{v,V}$ given by

$$\mathbf{r}_{v,V} = d_S \hat{\mathbf{z}} + \mathbf{r}_v^B + V d_B \hat{\mathbf{z}}, \quad (8)$$

where the index V refers to bulk cells and runs from 0 to N , the index v to bulk characteristic dipoles and runs from 1 to N_B . We choose $\mathbf{r}_1^B = \mathbf{0}$ always. We have shown in Ref. 1 that it is essential for the approach that the surface slabs always contain some dipole layers with geometric and electronic bulk configuration, the amount of which depends on the value of $|\alpha_B/\alpha_0|$, α_B being the bulk polarizability. So the boundaries between the subslabs are by construction always inside the bulklike area.

Now we define the normal modes by

$$\mathbf{p}_{v,V} = \sum_{m=1}^M \nu_m \mathbf{u}_{mv} e^{iq_m a V}, \quad (9)$$

$$\mathbf{u}_{mv} = e^{i\mathbf{k}_m \cdot \mathbf{r}_v^B} \mathbf{u}_{m1}, \quad (10a)$$

$$\mathbf{k}_m = (k_x, k_y, q_m). \quad (10b)$$

where the q_m correspond to the z component of the wave vector of the normal modes, the $\mathbf{u}_{mv}$ control the orientation of the normal modes in real space, and the ν_m their strength. We will further use the commensurability theorem introduced in Ref. 1:

The conditions under which this commensurability theorem is valid will be derived in Appendix B.

Inserting (6)–(10) into (1) yields, for any bulk characteristic dipole having indices (v, V) , the following equation:

$$\begin{aligned} & - \sum_{j=1}^{N_S} \left[\sum_{p,q} \vec{\mathbf{d}}_{pq} e^{-i\mathbf{k}_{pq} \cdot \mathbf{r}_j} e^{i\kappa_{pq} d_S} e^{i\kappa_{pq} d_B V} \right] \mathbf{p}_j + \sum_{m=1}^M \nu_m e^{iq_m V d_B} \vec{\mathbf{a}}(\mathbf{k}_m) \mathbf{u}_m \\ & - \sum_{m=1}^M \nu_m \sum_{w=1}^{N_B} \left[\frac{\vec{\mathbf{d}}_{pq} e^{-i\mathbf{k}_{pq} \cdot \mathbf{r}_w^B}}{1 - \exp[i(q_m - \kappa_{pq})d_B]} \right] e^{i\mathbf{k}_m \cdot \mathbf{r}_w^B} e^{i\kappa_{pq} d_B V} \mathbf{u}_m \\ & + \sum_{m=1}^M \nu_m \sum_{w=1}^{N_B} \left[\frac{\vec{\mathbf{d}}_{pq} e^{-i\bar{\mathbf{k}}_{pq} \cdot \mathbf{r}_w^B}}{1 - \exp[i(q_m + \kappa_{pq})d_B]} \right] e^{i\mathbf{k}_m \cdot \mathbf{r}_w^B} e^{-i(q_m + \kappa_{pq})N d_B} e^{-i\kappa_{pq} d_B V} \mathbf{u}_m \\ & - \sum_{j=N_S+1}^{N_S} \left[\sum_{p,q} \vec{\mathbf{d}}_{pq} e^{-i\bar{\mathbf{k}}_{pq} \cdot \mathbf{r}_j} e^{-i\kappa_{pq} d_S} e^{-i\kappa_{pq} d_B V} \right] \mathbf{p}_j = \mathbf{E}_0 e^{ik_z d_S} e^{ik_z d_B V}, \end{aligned} \quad (11)$$

where the index W has disappeared as a result of the summation, v has been put to 1 and $\vec{\mathbf{a}}(\mathbf{k}_m)$ is given by

$$\vec{\mathbf{a}}(\mathbf{k}_m) = \alpha_0^{-1} \left\{ \vec{\alpha}_B^{-1} \alpha_0 - \sum_{w=1}^{N_B} e^{i\mathbf{k}_m \cdot \mathbf{r}_w^B} \vec{\mathbf{f}}_{1w}^B + \sum_{w=1}^{N_B} e^{i\mathbf{k}_m \cdot \mathbf{r}_w^B} \left[\sum_{p,q} \left(\frac{\vec{\mathbf{d}}_{pq} e^{-i\mathbf{k}_{pq} \cdot \mathbf{r}_w^B}}{1 - \exp[i(q_m - \kappa_{pq})d_B]} + \frac{\vec{\mathbf{d}}_{pq} e^{-i\bar{\mathbf{k}}_{pq} \cdot \mathbf{r}_w^B}}{1 - \exp[-i(q_m + \kappa_{pq})d_B]} \right) \right] \right\}. \quad (12)$$

$\vec{\alpha}_B$ represents the bulk polarizability tensor. Furthermore, the $\vec{\mathbf{f}}_{1w}^B$ are subtensors of the type (6a), but calculated for two planes with characteristic dipoles belonging to the same bulk unit cell. In that case any explicit V or W dependence disappears.

Now (11) represents an infinite set of simultaneous equations. Coefficients belonging to the same exponential should be the same on the left and right. In addition, since $q_m \neq k_z$, one obtains from this requirement, as a first result, that

$$\vec{\mathbf{a}}(\mathbf{k}_m) \mathbf{u}_m = 0. \quad (13)$$

This equation yields only nontrivial solutions if

$$\text{Det}[\vec{\mathbf{a}}(\mathbf{k}_m)] = 0. \quad (14)$$

The normal-mode wave numbers q_m thus obtained characterize the dipole waves defined at the lattice points in the bulk of the solid. In principle there will be infinitely many solutions of (14). However, since we do not need to include the optical response of the surface in this reciprocal space treatment (Litzman has tried this Ref. 13), it is clear from (9) that it is sufficient to include only the normal modes being quasi-non-evanescent. These quasi-non-evanescent normal modes are defined as

the ones having a decay length larger than the width of the surface region, which is to be defined in practice (it will never be much larger than about ten dipole layers). This way the number of normal modes has been restricted to four, namely two in the upward direction and two in the downward direction. Since we have no optical activity, we can set

$$q_3 = -q_1, \quad q_4 = -q_2. \quad (15a)$$

It is then easy to prove that for the corresponding normal-mode eigenvectors, which follow from (13), we have

$$\mathbf{u}_3 = \mathbf{u}_1, \quad \mathbf{u}_4 = \mathbf{u}_2. \quad (15b)$$

Although the quasi-non-evanescent normal-mode wave numbers q_m , as they characterize discrete-dipole waves, relate to different physical quantities, such as the Fresnel wave number q_F , which represent the macroscopic electric fields inside the solid, it can be shown that these wave numbers have the same numerical values up to $O(k^3)$ (see below). The difference between q_1 and q_2 , which is also of the third order in k , accounts for the spatial dispersion in the bulk.^{14,15} Furthermore, it has been proved by Litzman and co-workers¹⁶ that for a semi-

infinite bulk-truncated cubic lattice and perpendicular incident light the discrete theory reduces to the classical Snell-Descartes law and Fresnel formulas in the long-wavelength limit.

From (11) one equation for each pair (p, q) will be obtained, but for optics it suffices to consider the $(0, 0)$ equations only. Through the use of a projection technique¹ the interaction equations for the bulk reduce to

$$\begin{aligned} -\sum_{j=1}^{N_S^I} (\mathbf{g}_s \cdot \vec{\mathbf{d}}_{00}) e^{-i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{p}_j - \nu_1(\mathbf{g}_s \mathbf{g}_1) - \nu_3(\mathbf{g}_s \mathbf{g}_3) &= \mathbf{g}_s \cdot \mathbf{E}_0, \\ -\sum_{j=1}^{N_S^I} (\mathbf{g}_p \cdot \vec{\mathbf{d}}_{00}) e^{-i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{p}_j - \nu_2(\mathbf{g}_p \mathbf{g}_2) - \nu_4(\mathbf{g}_p \mathbf{g}_4) &= \mathbf{g}_p \cdot \mathbf{E}_0, \\ \nu(\mathbf{g}_s \mathbf{g}_1) + \nu_3(\mathbf{g}_s \mathbf{g}_3) - \sum_{j=N_S^I+1}^{N_S} (\mathbf{g}_s \cdot \vec{\mathbf{d}}_{00}) e^{-i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{p}_j &= 0, \\ \nu_2(\mathbf{g}_p \mathbf{g}_2) + \nu_4(\mathbf{g}_p \mathbf{g}_4) - \sum_{j=N_S^I+1}^{N_S} (\mathbf{g}_p \cdot \vec{\mathbf{d}}_{00}) e^{-i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{p}_j &= 0, \end{aligned} \quad (16)$$

with

$$\mathbf{g}_m = \sum_{w=1}^{N_B} \vec{\mathbf{d}}_{00} e^{-ik_z d_S} \left[\frac{e^{-i(k_z - q_m)z_w^B}}{1 - e^{-i(k_z - q_m)d_B}} \right] \mathbf{u}_m, \quad (17a)$$

$$\mathbf{g}_m = \sum_{w=1}^{N_B} \vec{\mathbf{d}}_{00} e^{ik_z d_S} \left[\frac{e^{i(k_z + q_m)(z_w^B + Nd_B)}}{1 - e^{i(k_z + q_m)d_B}} \right] \mathbf{u}_m, \quad (17b)$$

$$\mathbf{g}_s = \vec{\mathbf{d}}_{00} \cdot \mathbf{u}_1, \quad \mathbf{g}_p = \vec{\mathbf{d}}_{00} \cdot \mathbf{u}_2, \quad (17c)$$

$$\mathbf{g}_s = \vec{\mathbf{d}}_{00} \cdot \mathbf{u}_3, \quad \mathbf{g}_p = \vec{\mathbf{d}}_{00} \cdot \mathbf{u}_4. \quad (17d)$$

Here we made use of the orthogonality of the vectors $\mathbf{g}_m$ and $\mathbf{g}_{s,p}$ and their reflected counterparts (see the Appendix of Ref. 1).

For any characteristic dipole i , located in the first subslab, we obtain the corresponding interaction equation:

$$\vec{\alpha}_i^{-1} \mathbf{p}_i - \alpha_0^{-1} \left[\sum_{j=1}^{N_S^I} \vec{\mathbf{f}}_{ij} \mathbf{p}_j - \sum_{m=1}^M \mathbf{g}_m^i \nu_m - \sum_{j=N_S^I+1}^{N_S} \vec{\mathbf{f}}_{ij} \mathbf{p}_j \right] = \mathbf{E}_i, \quad (18)$$

$$\begin{aligned} \mathbf{P}(\mathbf{k}) &= \sum_{j=1}^{N_S} e^{-i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{p}_j + e^{ik_z d_S} \sum_{m=1}^4 \left[\sum_{w=1}^{N_B} e^{i(k_z + q_m)z_w^B} \left[\frac{1 - e^{i(k_z + q_m)Nd_B}}{1 - e^{i(k_z + q_m)d_B}} \right] \right] \nu_m \mathbf{u}_m, \\ \mathbf{P}^T &= \mathbf{P}(\mathbf{k}), \quad \mathbf{P}^R = \mathbf{P}(\mathbf{k}). \end{aligned} \quad (23)$$

The summation over the two surface layers has been combined in this expression. The expressions for the reflectivity and transmittivity coefficients of the thick dielectric slab then follow immediately from

$$r = \left[\frac{ik^2}{2\epsilon_0 \beta k_z a^2} \right] \left[\frac{\mathbf{E}_0 \cdot \mathbf{P}^R}{|\mathbf{E}_0|^2} \right], \quad (24a)$$

$$\begin{aligned} \mathbf{g}_m^i &= \sum_{v=1}^{N_B} \sum_{p,q} \vec{\mathbf{d}}_{pq} e^{i\mathbf{k}_{pq} \cdot (\mathbf{r}_i - \mathbf{r}_{Bv})} e^{i\kappa_{pq} d_S} \\ &\times \left[\frac{1 - e^{i(q_m + \kappa_{pq})d_B N}}{1 - e^{i(q_m + \kappa_{pq})d_B}} \right] e^{i\mathbf{k}_m \cdot \mathbf{r}_{Bv}} \mathbf{u}_m, \end{aligned} \quad (19)$$

where $\vec{\mathbf{f}}_{ii} = \vec{\mathbf{c}}(\mathbf{k})$ (see Appendix A).

The solution of the set of interaction equations (16)–(19) yields the unknown $\mathbf{p}_i^I$, ν_m , and $\mathbf{p}_i^II$, which are, respectively, N_S^I complex vectors, four complex mode strengths, and N_S^II complex vectors.

Now we will derive the expressions for the reflection and transmission coefficients. From Ref. 1 we know that the dipole field $\mathbf{E}_{\text{dip}}$ at any point $\mathbf{r}$ follows from

$$\mathbf{E}_{\text{dip}}(\mathbf{r}) = \sum_{i=1}^{N_S} \vec{\mathbf{f}}_i(\mathbf{r}) \mathbf{p}_i + \sum_{v=1}^{N_B} \sum_{V=0}^{N-1} \vec{\mathbf{f}}_{v,V}(\mathbf{r}) \mathbf{p}_{v,V}. \quad (20)$$

The reflection and transmission coefficients will be obtained from the far-field expression of (20). These remote fields have to be found from the transfer tensor (6a), which is calculated by means of the threefold integral transform. For the transmitted remote fields, z will always be larger than the z coordinate of any of the dipole sites (remember the location of the slab in space). Furthermore, as z approaches infinity we have

$$\kappa_{pq} = k_z \Rightarrow e^{i\kappa_{pq}(z - z_i)} = e^{ik_z(z - z_i)} \quad (p, q) = (0, 0), \quad (21)$$

$$\kappa_{pq} = i|\kappa_{pq}| \Rightarrow e^{i\kappa_{pq}(z - z_i)} = e^{-|\kappa_{pq}|(z - z_i)}, \quad (p, q) \neq (0, 0),$$

and this last expression will go to zero as z goes to infinity. So for remote fields only the $(0, 0)$ term has to be taken into account. Analogous arguments can be used for the reflected remote fields. Taking this into account and inserting (9) and (10) into (20) we get, for reflection and transmission, respectively,

$$\mathbf{E}^R(\mathbf{r}, t) = \vec{\mathbf{d}}_{00} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{P}^R, \quad (22a)$$

$$\mathbf{E}^T(\mathbf{r}, t) = \mathbf{E}_{\text{ext}}(\mathbf{r}, t) + \vec{\mathbf{d}}_{00} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{P}^T, \quad (22b)$$

where the vectors $\mathbf{P}^R$ and $\mathbf{P}^T$ are defined through

$$t = 1 + \left[\frac{ik^2}{2\epsilon_0 \beta k_z a^2} \right] \left[\frac{\mathbf{E}_0 \cdot \mathbf{P}^T}{|\mathbf{E}_0|^2} \right]. \quad (24b)$$

In (24b) it has tacitly been understood that the slab contribution to the transmitted field has the same polarization as the exciting light beam, which is true for the cases studied in this article. It is at this point, the calculation

of the reflection and transmission coefficients, that the differences between this theory and the d -parameter theory described in Ref. 4 are most pronounced. Chen and Schaich try to incorporate into their calculation of these optical coefficients, the spatial dispersion of the surface region by introducing their d parameters. So two additional parameters $d_{\perp}$ and $d_{\parallel}$ are used to describe the surface local field effects, while from (9) it immediately follows that the number of complex values q_m needed to do this, in principle, is infinite. It therefore seems that their method is much less flexible in taking into account large spatial variations at the surface, a fact which has al-

ready been noticed in Ref. 3. The theory derived above gives an exact, fully retarded description of the optical response of a thick dielectric slab on the surfaces of which a (sub)monolayer has been adsorbed. The great advantage of this approach and the way we implemented it is the flexibility of the method to cope with large and arbitrary surface systems, as has been shown recently by us for the case of the reconstruction of the Si(110) surface.¹⁷

Flow chart for the calculation of the reflection coefficient for a thick slab:

III. NUMERICAL CALCULATIONS

We will now apply the theory developed above to the case of the ir absorption of a monolayer of CO physisorbed onto a NaCl(100) surface. In the first place we would like to model the absorption spectrum as measured by Richardson *et al.*⁵ To do this we first need to determine what our input parameters, the geometry, and polarizabilities of both the CO overlayer and the NaCl sub-

strate are. Because the system we describe is supposed to be a model system for physisorption, for CO we will try to remain as close as possible to the gas-phase values and for NaCl as close as possible to the bulk values. The NaCl bulk cell is cubic, has a lattice constant $a = 5.64 \text{ \AA}$,¹⁸ and contains eight representing dipoles with isotropic polarizabilities given by¹⁹

$$\alpha(\text{Cl}^-) = 3.08 \text{ \AA}^3, \quad (25a)$$

$$\alpha(\text{Na}^+) = 0.16 \text{ \AA}^3. \quad (25b)$$

Here we have taken the theoretical value of $\alpha(\text{Na}^+)$ since calculations show that this quantity is rather insensitive to the environment of the Na^+ ion, whereas $\alpha(\text{Cl}^-)$ is calculated using $\alpha(\text{NaCl}) = \alpha(\text{Na}^+) + \alpha(\text{Cl}^-) = 3.24 \text{ \AA}^3$,¹⁹ which is a good approximation for alkali-halide crystals. Now, we will describe every atom (Cl^- , Na^+) as one dipole in the surface part of the calculation; in the bulk part, NaCl molecules, situated at the position of the Cl^- ion, will be used as polarizable units.

The CO molecules are adsorbed on top of the Na^+ ions⁵ at a height d and the polarizability tensor of a CO molecule will be given by $\tilde{\alpha}(\text{CO}) = \tilde{\alpha}_e + \tilde{\alpha}_v$, where α_e is the electronic polarizability tensor with²⁰

$$\alpha_{xx}^e = \alpha_{yy}^e = 1.79 \text{ \AA}^3, \quad \alpha_{zz}^e = 2.32 \text{ \AA}^3. \quad (26a)$$

The other components equal zero. α_v is the vibrational polarizability tensor and it contains only one nonzero component, namely

$$\alpha_{zz}^v = \alpha_v [1 - (\omega^2 + i\omega\gamma)/\bar{\omega}^2]^{-1}, \quad (26b)$$

where α_v is the static vibrational polarizability. We will set γ equal to 0.42 cm^{-1} , and choose $\bar{\omega}$ so as to reproduce, respectively, the broadening and location of the resonance at 55 K .⁵ All the other components of $\tilde{\alpha}(\text{CO})$ equal 0.

We investigate if it is possible with these parameters to reproduce the experimental spectrum of Ref. 5, taking the gas-phase value of $\alpha_v = 0.053 \text{ \AA}^3$ (Ref. 21) and the values of d quoted in literature.^{4,22} Since Richardson *et al.* claim that in the temperature range $5\text{--}55 \text{ K}$ the integrated absorbance remains invariant, we tried to fit this parameter. We calculate the absorbance for light, incident at an angle of 60° . Here and further in this section, we will always deal with p -polarized light unless explicitly stated otherwise. We use the formula¹¹

$$A_p = 2 \log_{10}(T_0/T), \quad (27)$$

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

$$\tilde{A}_p = \int_{-\infty}^{+\infty} A_p(\omega) d\omega \quad (28)$$

is calculated numerically over a large enough energy interval. Chen and Schaich⁴ calculate the absorbance of a slab as twice the absorbance of a semi-infinite NaCl crystal with a CO monolayer. We varied the thickness of the slab over one wavelength of light in this frequency region and found that the integrated absorbance oscillates, giving the results an uncertainty of about 5%, since in the original article of Richardson and Ewing²³ the thickness of the NaCl crystal is given as "about 3 mm."

If we take for the distance between the CO overlayer and the NaCl substrate the value used in Ref. 4, $d = 3.3 \text{ \AA}$, we obtain a spectrum yielding an integrated absorbance $\tilde{A}_p = 0.0245 \text{ cm}^{-1}$. The experimentally measured value equals 0.019 cm^{-1} ,⁵ 22.4% below the theoretical value. Taking $d = 2.98 \text{ \AA}$ (Ref. 22) gives $\tilde{A}_p = 0.0239 \text{ cm}^{-1}$. So it appears that neither of these

two values generates the correct value of the integrated absorbance. For reasons of comparison we repeat this calculation with the same input parameters and geometric arrangement used by Chen and Schaich.⁴ So this time we consider a fcc lattice of NaCl molecules with a frequency-independent polarizability $\alpha_B = 3.62 \text{ \AA}^3$. The height of the adsorbate dipoles again is $3.3 \text{ \AA}$, their electronic polarizability is given by $\alpha_e = 2.33 \text{ \AA}^3$, and their static vibrational polarizability is given by $\alpha_v = 0.053 \text{ \AA}^3$. The results can be found in Table I where we give the integrated absorbance $\tilde{A}_p$ and the value of $\bar{\omega}$ needed to obtain an absorption peak at 2155.09 cm^{-1} . We see that there are indeed significant quantitative differences between the predictions of the two approaches. The fact that our results are closer to the experimental values is possibly due to our exact and retarded calculation of the local fields at the surface, while the model described in (Ref. 14) is based on a perturbative approach and uses the electrostatic limit to calculate the dipole field.

We now return, for the rest of the paper, to the more realistic input parameters and configuration we gave at the beginning of this section. In order to see what effect a change in α_v or d has, we plotted in Fig. 1(a) the integrated absorbance for $d = 3.3 \text{ \AA}$ as a function of α_v and the same quantity for $\alpha_v = 0.053 \text{ \AA}^3$ as a function of d in Fig. 1(b). From the first curve we learn that, in this region, the integrated absorbance depends linearly on α_v , a result that is also obtained in Ref. 4. Since we know¹ that the absorbance of the i th layer of a slab is given by

$$A_i = - \frac{k^2}{\beta k_z \epsilon_0 a^2 |\mathbf{E}_0|^2} \text{Im}(\mathbf{E}_{\text{loc},i}^* T_i(\tilde{\alpha}_i)^{-1} \mathbf{E}_{\text{loc},i}), \quad (29)$$

and since only the two CO layers absorb radiation at this frequency (absorption by the NaCl lattice due to surface phonons occurs at much lower frequencies; see, e.g., Ref. 24), we have to conclude that the internal field at the position of the CO molecule depends only slightly on the vibrational polarizability. Figure 1(b) shows through (29) that the value of the internal field is very sensitive to the distance of the CO monolayer to the NaCl substrate, which confirms the findings in Ref. 25. There is a minimum in $\tilde{A}_p$ at a distance of about $1.82 \text{ \AA}$ ($d/a \approx 0.32$). We expect that below this distance the linear relation we found in Fig. 1(a) does not hold anymore, but since we are dealing with physically unrealistic small values of d , we did not study this phenomenon any further.

So in order to arrive at an agreement between theory and experiment, we find that we can decrease the value of α_v and/or that of d , an option which has not been considered by other authors in this field.^{4,5,7} To get a feeling

TABLE I. Comparison between the results of this model and those of Ref. 4. The input parameters are those used in Ref. 4 (see text).

	Ref. 4	This work
$\tilde{A}_p$	0.028 cm^{-1}	0.0243 cm^{-1}
$\bar{\omega}$	2148.6 cm^{-1}	2148.99 cm^{-1}

for the magnitude of the possible changes, we plotted in Fig. 2 the relation between α_v and d , which gives the experimental value of the integrated absorbance. We see that for the gas-phase value of α_v ($0.053 \text{ \AA}^3$), there is no d yielding the correct $\tilde{A}_p$, a fact that could already be expected from Fig. 1(b). In order to explain a possible origin of the changes we calculated, using Lambert's expansion parameters,²⁶ the change in α_v caused by the influence of the static electric field of the NaCl lattice. We find that the electric-field-dependent change in the CO vibrational polarizability is given by

$$\Delta\alpha_v = (1.025 \times 10^{-13} E) \text{ \AA}^3,$$

with E the magnitude of the static electric field at the site of the CO molecule. We calculated in a classical way (taking only electromagnetic interactions into account) $E \cong 3 \times 10^{10} \text{ V/m}$. Using this value, we get a correction

FIG. 1. (a) Relation between the integrated absorbance of two NaCl slabs, covered on both sides by a CO monolayer at a distance of $3.3 \text{ \AA}$ from the substrate, and the static vibrational polarizability of a CO molecule. The incident light wave is p polarized and incident under an angle of 60° . (b) The integrated absorbance of two NaCl slabs, covered on both sides by a CO monolayer, as a function of the distance d of the CO molecules to the substrate. The static vibrational polarizability of a CO molecule is $0.053 \text{ \AA}^3$. The incident light wave is p polarized and incident under an angle of 60° .

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

of about 5%, which is not only too small to account for the change in absorbance but, furthermore, it is in the wrong direction, i.e., it increases α_v .

We also establish in Fig. 3 the relation between $\bar{\omega}$ and d (and thus α_v) for an integrated absorbance of 0.019 cm^{-1} . Combining the results of Figs. 2 and 3 yields for every value of d a unique set $(\alpha_v, \bar{\omega})$ producing an absorption peak in the ir spectrum at 2155.09 cm^{-1} with an integrated absorbance of 0.019 cm^{-1} .

The value of $\bar{\omega}$ is determined by two effects: the change in the coupling strength between the C and O atoms upon adsorption on the NaCl substrate, and the influence of the CO molecules in the monolayer on each other. Both effects are static and since the first one will affect the zz component of the static vibrational polarizability directly it will be the largest of the two. By comparing our values of $\bar{\omega}$ with the gaseous one (2143.3 cm^{-1}) we can conclude that the static interactions are responsible for a frequency shift $\Delta\bar{\omega}_{\text{stat}} = (6.95 \pm 0.25) \text{ cm}^{-1}$. The dynamical contribution to the frequency shift (i.e., the contribution due to the interaction with the incident ir light) is $\Delta\bar{\omega}_{\text{dyn}} = (5.25 \pm 0.25) \text{ cm}^{-1}$. The exact value of both fre-

FIG. 3. Relation between $\bar{\omega}$ and d for an integrated absorbance $\tilde{A}_p$ of 0.019 cm^{-1} .

quency shifts of course depends on the unknown d . Zecchina, Scarano, and Garrone⁷ conclude from a study of the isotope effect on the ir spectroscopy of CO monolayers on sintered NaCl films that these static effects are responsible for a frequency shift of -6 cm^{-1} , and there is no point on our curve which could account for such a value. However, their analysis of the CO-NaCl interaction is based on the modified Hamaker equation,^{27,28} so they assume that there is no dynamical coupling effect between the CO and its substrate, an assumption which we showed to be erroneous [see Fig. 1(b)]. This is also the reason for the very low value of the vibrational polarizability $\alpha_v = 0.0235 \text{ \AA}^3$ —they need to fit their data.

Now in order to test the convergence of the model described in Sec. II, we will examine the microscopy of the system. First we calculated the values of the normal-mode wave numbers q_m of the NaCl bulk. We found that

$$q_1 - q_F = (4.489\,533 \times 10^1) a^2 k^3 \text{ \AA}^{-1}, \quad (30a)$$

$$q_2 - q_F = (3.567\,393 \times 10^{-1}) a^2 k^3 \text{ \AA}^{-1}, \quad (30b)$$

confirming the claim we made in Sec. II that the results of our discrete theory and the classical continuum theory are identical up to $O(k^3)$. Since it also appears that for s -polarized incident light $\nu_2 = \nu_4 = 0$, and for p -polarized light $\nu_1 = \nu_3 = 0$, the different values of the coefficient in (30a) and (30b) will give rise to bulk spatial dispersion effects. Similar conclusions were attained in Ref. 14. In Table II we give the absorbance of the first CO monolayer, calculated using (29), for a point on the curve of Fig. 2, namely $\alpha_v = 0.047 \text{ \AA}^3$, $d = 0.372a = 2.097 \text{ \AA}$, at the energy of 2155.09 cm^{-1} , i.e., the top of the absorption peak (see Fig. 4). We vary the number of NaCl dipole layers in the two surface cells. (N_S^{II} equals N_S^I here.) We see that without including NaCl dipole layers into the surface subslabs, we get a value of the absorbance that is much too small. The reason of this effect can be seen in Table III, where we give the dipole strength of the first eight layers of the first surface slab relative to $p_0 = \alpha_0 E_0 = \alpha_0 |E_0|$, for different values of N_S^I . In order to be able to compare between the bulk and the surface dipoles we took here a NaCl molecule as a polarizable unit also in the surface slab. This decreases the value of the absorbance by about 6%, but it does not affect the point we want to make here. We see that if the bulk slab starts immediately at the first NaCl layer, the strength of the dipoles in the first two NaCl layers are underestimated due to the normal-mode composition (9), as is the influence of these dipoles onto the CO monolayer. Through (29) this results in a value of the absorbance that is too small. We

TABLE II. Convergence test. Local absorbance A_p^I of the first CO monolayer as a function of the number of Na^+ and Cl^- representing dipoles in the first surface slab.

	A_p^I
0	$1.372\,059 \times 10^{-2}$
4	$2.989\,996 \times 10^{-2}$
8	$2.989\,396 \times 10^{-2}$
12	$2.989\,393 \times 10^{-2}$

FIG. 4. Absorption spectrum of two NaCl slabs, covered on both sides by a CO monolayer with $\alpha_v = 0.047 \text{ cm}^{-1}$ and $d = 2.098 \text{ \AA}$.

further plot in Fig. 5 the absolute value of the dipole strengths of Na^+ and Cl^- in the first few layers of a slab with adsorbed CO, relative to the same quantity of a slab without CO. We see that after three NaCl layers there is no change anymore in this quantity. The Na^+ atom in the first layer is affected more than the Cl^- atom by the presence of the CO overlayer, which could be expected because the CO molecules are closer to the anion. However, due to the much smaller value of the Na^+ polarizability (25), it is still the cation which will be responsible for most of the occurring effects. We can conclude that the spatial dispersion due to the presence of the CO layer extends into the NaCl substrate over a distance of about $3a = 16.92 \text{ \AA}$.

We further tested if any decisive conclusion could be drawn from the location of the Brewster angle at the peak energy for different values of α_v , giving the experimental value of the integrated absorbance [also for two points on the curve of Fig. 2: $(\alpha_v, d) = (0.041 \text{ \AA}^3, 0.595a)$ and $(0.047 \text{ \AA}^3, 0.372a)$]. In Fig. 6 we see that, as expected, the reflectance exhibits an oscillation with increasing angle of incidence. Of course these oscillations will not be observed experimentally, since this standing-wave pattern depends on the two surfaces being parallel to better than a fraction of the wavelength. This condition can only be met theoretically and always will be met due to parallel translational symmetry. Also, small variations in the angle of incidence ϑ can extinguish this interference pattern. But even if we discard these experimental difficulties for the moment, a comparison between the calculated spectra of $\alpha_v = 0.047$ and $0.041 \text{ \AA}^3$ reveals that in both cases the same Brewster angle is found. Furthermore, we compared the reflectance and transmittance spectra for both values of α_v , as well as the spectra of their ellipsometric angles ψ and Δ . We found that the deviation is 5% at the most. Taking into account that there is a 10% experimental error in the measured integrated absorbance, we conclude from this that two different settings of $(\alpha_v, d, \bar{\omega})$, which give the same integrated absorbance, exhibit the same macroscopic be-

TABLE III. Convergence test. NaCl dipole strength of the first eight NaCl surface layers as a function of N_S^I , for a NaCl slab with a CO overlayer.

$10^2 p/p_0$	N_S^I	0	2	4	6	8
NaCl ₁	1.641 446	5.838 116	5.838 116	5.838 116	5.838 116	5.838 116
NaCl ₂	1.641 464	1.811 663	1.812 368	1.812 368	1.812 368	1.812 368
NaCl ₃	1.641 481	1.635 827	1.627 636	1.627 636	1.627 636	1.627 636
NaCl ₄	1.641 498	1.635 845	1.636 398	1.636 398	1.636 398	1.636 398
NaCl ₅	1.641 516	1.635 862	1.635 867	1.635 832	1.635 832	1.635 831
NaCl ₆	1.641 534	1.635 879	1.635 885	1.635 887	1.635 887	1.635 887
NaCl ₇	1.641 551	1.635 896	1.635 902	1.635 902	1.635 902	1.635 902
NaCl ₈	1.641 568	1.635 914	1.635 919	1.635 919	1.635 919	1.635 919

havior, within experimental error. However, all these macroscopically equivalent cases may and do have microscopically different behavior.

We can conclude that 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. If we use the gas-phase value of α_v , we end up with a distance d which is so short that it is unlikely that α_v would not have changed. On the other hand, if we use a value of the distance quoted in literature [3.3 Å (Ref. 4) and 2.98 Å (Ref. 21)], we have to change α_v so much that the assumption of virtually unmodified wave functions becomes untenable. 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/or its distance to this surface will decrease with respect to the usual values. This means that the original assumptions of most authors who studied this system, that it is a model system of physisorption, i.e., that the bonding is dominated by classical electrostatic forces and the properties of the monolayer will remain close to their gas-phase values, cannot be persisted, a view which is sustained by the high value of the heat of adsorption found by Gevitzman, Kozirovski, and Folman.²² This of course makes the determination of the

actual combination of $(\alpha_v, d, \bar{\omega})$ for a system like the one we studied very difficult. However, if the distance d can be determined experimentally using techniques other than ir spectroscopy, the theory presented here is capable of predicting a value of the vibrational polarizability α_v , which fits the experimental ir spectra. We also believe that a quantum-mechanical calculation of α_v , taking into account the interaction of a CO molecule with the NaCl substrate, but also the mutual interactions between the CO molecules, would be desirable.

FIG. 5. Absolute value of the dipole strength of Na⁺ and Cl⁻ of a NaCl slab covered with CO, relative to the same quantity of a slab without CO, as a function of the layer number.

FIG. 6. Reflection for p -polarized light of a NaCl slab as a function of the angle of incidence (upper curve). The same quantity for a NaCl slab covered on both sides of a CO monolayer (lower curve). The values of α_v and d correspond to a point on the curve of Fig. 2, namely $(\alpha_v, d) = (0.047 \text{ Å}^3, 0.372a)$. The photon energy is 2155.09 cm^{-1} .

APPENDIX A

We will derive here the exact expressions for the transfer tensors, using Ewald's onefold integral transform:⁸

$$\vec{f}_{ij} = a^3 [(\nabla \nabla^T + k^2) S_j(\mathbf{r}, \mathbf{k})]_{\mathbf{r}=\mathbf{r}_i} . \quad (\text{A1})$$

There are two reasons for doing this. If we try to calculate the transfer tensor $\vec{f}_{ij}$ using (13), we see that whenever $z_i = z_j$, the series will not converge. Furthermore, the onefold integral transform appears to be faster convergent than the threefold one as long as $|z_i - z_j| \leq z_0$, z_0 being of the order of magnitude of a .

1. Interplanar near

Before we apply the operator $(\nabla \nabla^T + k^2)$ to the lattice sum $S_j(\mathbf{r}, \mathbf{k})$, we will transform this sum to a form which is faster convergent. Starting with the expression (A1), we use the integral representation

$$\frac{e^{ikr}}{r} = \frac{2}{\sqrt{\pi}} \int_{(0), \Gamma}^{\infty} \exp \left[-r^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] d\epsilon . \quad (\text{A2})$$

A proof of this identity and the form of the integration contour can be found in Ref. 8.

Applying this to the expression (11c) we get

$$S_j(\mathbf{r}, \mathbf{k}) = \frac{2}{\sqrt{\pi}} \sum_{n,m} e^{i\mathbf{k} \cdot \mathbf{s}_{nm}} \int_{(0), \Gamma}^{\infty} \exp \left[-|\mathbf{r} - \mathbf{r}_{j,nm}|^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] d\epsilon \quad (\text{A3a})$$

$$= \frac{2}{\sqrt{\pi}} e^{i\mathbf{k} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}^{\parallel})} \int_{(0), \Gamma}^{\infty} \exp \left[-(z - z_j)^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] \sum_{n,m} \exp[i\mathbf{k} \cdot (\mathbf{r}_{j,nm}^{\parallel} - \mathbf{r}^{\parallel}) - (\mathbf{r}^{\parallel} - \mathbf{r}_{j,nm}^{\parallel})^2 \epsilon^2] d\epsilon , \quad (\text{A3b})$$

with $\mathbf{r}_{j,nm}$ given by (1). It is now very straightforward to prove that

$$f(\mathbf{r}^{\parallel}) = \sum_{n,m} \exp[i\mathbf{k} \cdot (\mathbf{r}_{j,nm}^{\parallel} - \mathbf{r}^{\parallel}) - (\mathbf{r}^{\parallel} - \mathbf{r}_{j,nm}^{\parallel})^2 \epsilon^2] \quad (\text{A4})$$

is periodic in the two-dimensional surface lattice, so it can be expanded in Fourier series, yielding

$$f(\mathbf{r}^{\parallel}) = \frac{\pi}{\beta a^2 \epsilon^2} \sum_{p,q} \exp \left[\frac{-\mathbf{k}_{pq}^{\parallel 2}}{4\epsilon^2} \right] e^{i\mathbf{g}_{pq}^{\parallel} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}^{\parallel})} . \quad (\text{A5})$$

We will prove this now. If $f(\mathbf{r}^{\parallel}) = f(\mathbf{r}^{\parallel} + \mathbf{s}_{nm})$, then

$$f(\mathbf{r}^{\parallel}) = \sum_{p,q} \tilde{f}(p, q) \exp(i\mathbf{g}_{pq}^{\parallel} \cdot \mathbf{r}^{\parallel}) \quad (\text{A6})$$

with

$$\tilde{f}(p, q) = \frac{1}{|\mathbf{s}_1 \times \mathbf{s}_2|} \int_{1\text{ws}_{\parallel}} f(\mathbf{r}^{\parallel}) \exp(-i\mathbf{g}_{pq}^{\parallel} \cdot \mathbf{r}^{\parallel}) d\mathbf{r}^{\parallel} , \quad (\text{A7})$$

where the integration goes over one surface Wigner-Seitz cell whose area is $|\mathbf{s}_1 \times \mathbf{s}_2| = \beta a^2$. Now putting (A4) into (A7) yields

$$\begin{aligned} \tilde{f}(p, q) = \frac{1}{\beta a^2} \sum_{n,m} \int_{1\text{ws}_{\parallel}} \exp[i\mathbf{k} \cdot (\mathbf{r}_{j,nm}^{\parallel} - \mathbf{r}^{\parallel}) \\ - (\mathbf{r}^{\parallel} - \mathbf{r}_{j,nm}^{\parallel})^2 \epsilon^2] \\ \times \exp(-i\mathbf{g}_{pq}^{\parallel} \cdot \mathbf{r}^{\parallel}) d\mathbf{r}^{\parallel} , \end{aligned} \quad (\text{A8})$$

and after a change of integration variable

$$\begin{aligned} \tilde{f}(p, q) = \frac{1}{\beta a^2} e^{-i\mathbf{g}_{pq}^{\parallel} \cdot \mathbf{r}^{\parallel}} \\ \times \int_{-\infty}^{+\infty} \exp(-i\mathbf{k}_{pq}^{\parallel} \cdot \mathbf{r}'^{\parallel} - \mathbf{r}'^{\parallel 2} \epsilon^2) d\mathbf{r}'^{\parallel} . \end{aligned} \quad (\text{A9})$$

We then solve the complex contour integration, which gives

$$\tilde{f}(p, q) = \frac{\pi}{\beta a^2 \epsilon^2} \exp \left[\frac{-\mathbf{k}_{pq}^{\parallel 2}}{4\epsilon^2} \right] e^{-i\mathbf{g}_{pq}^{\parallel} \cdot \mathbf{r}^{\parallel}} . \quad (\text{A10})$$

Putting this into (A6) gives the expression (A5). Equations (A4) and (A5) together then gives us the following expression for $S_j(\mathbf{r}, \mathbf{k})$:

$$\begin{aligned} S_j(\mathbf{r}, \mathbf{k}) = \frac{2\sqrt{\pi}}{\beta a^2} \sum_{p,q} e^{i\mathbf{k}_{pq}^{\parallel} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}^{\parallel})} \\ \times \int_{(0), \Gamma}^{\infty} \exp \left[\frac{\kappa_{pq}^2}{4\epsilon^2} - (z - z_j) \right] \frac{d\epsilon}{\epsilon^2} . \end{aligned} \quad (\text{A11})$$

Now the sum (A3a) over the two-dimensional crystal lattice is rapidly converging for large values of ϵ , while the sum (A11) over the two-dimensional reciprocal lattice converges rapidly for sufficiently small values of ϵ . We therefore set

$$S_j(\mathbf{r}, \mathbf{k}) = S_j^I(\mathbf{r}, \mathbf{k}) + S_j^{II}(\mathbf{r}, \mathbf{k}) , \quad (\text{A12})$$

where $S_j^I(\mathbf{r}, \mathbf{k})$ is the expression (A3a), but with integration from a real positive parameter E to infinity, while $S_j^{II}(\mathbf{r}, \mathbf{k})$ is the expression (A11), but with integration from (0) to E .

Now we use the identities^{8,29}

$$\begin{aligned} & \frac{2}{\sqrt{\pi}} \int_E^\infty \exp \left[-r^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] d\epsilon \\ &= \frac{1}{2r} \left[e^{ikr} \operatorname{erfc} \left[rE + \frac{ik}{2E} \right] + e^{-ikr} \operatorname{erfc} \left[rE - \frac{ik}{2E} \right] \right] \end{aligned} \quad (\text{A13a})$$

and

$$\begin{aligned} & \frac{2}{\sqrt{\pi}} \int_{(0)}^E \exp \left[\frac{\kappa^2}{4\epsilon^2} - \epsilon^2 r^2 \right] \frac{d\epsilon}{\epsilon^2} \\ &= \frac{-1}{ik} \left[e^{ikr} \operatorname{erfc} \left[-rE - \frac{ik}{2E} \right] \right. \\ & \quad \left. + e^{-ikr} \operatorname{erfc} \left[rE - \frac{ik}{2E} \right] \right], \end{aligned} \quad (\text{A13b})$$

where k and r are arbitrary real variables, κ is an arbitrary complex variable which obeys $\operatorname{Re}(\sqrt{\kappa}) > 0$ and erfc is the complementary error function. Putting this into (A3a) and (A11) yields the final expression for $S_j(\mathbf{r}, \mathbf{k})$:

$$\begin{aligned} S_j(\mathbf{r}, \mathbf{k}) = & \frac{i\pi}{\beta a^2} \sum_{p,q} \frac{e^{i\mathbf{k}_{pq} \cdot \mathbf{r}^\parallel}}{\kappa_{pq}} \left[e^{i\kappa_{pq}(z-z_j)} \operatorname{erfc} \left[-\frac{i\kappa_{pq}}{2E} - (z-z_j)E \right] + e^{-i\kappa_{pq}(z-z_j)} \operatorname{erfc} \left[-\frac{i\kappa_{pq}}{2E} + (z-z_j)E \right] \right] \\ & + \frac{1}{2} \sum_{n,m} \frac{e^{i\mathbf{k} \cdot \mathbf{s}_{nm}}}{|\mathbf{r} - \mathbf{r}_{j,nm}|} \left[e^{ik|\mathbf{r} - \mathbf{r}_{j,nm}|} \operatorname{erfc} \left[|\mathbf{r} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E} \right] + e^{-ik|\mathbf{r} - \mathbf{r}_{j,nm}|} \operatorname{erfc} \left[|\mathbf{r} - \mathbf{r}_{j,nm}|E - \frac{ik}{2E} \right] \right]. \end{aligned} \quad (\text{A14})$$

Now we can find the components of the transfer tensor $\vec{f}_{ij}$ from (A14) by applying the vector operator $(\nabla \nabla^T + k^2)$ to it and evaluating it at the position $\mathbf{r} = \mathbf{r}_i$. The calculation of $\vec{f}_{ij}$ then follows in a straightforward way:

$$\begin{aligned} f_{ij}^{\mu\nu} = & \frac{i\pi}{\beta a^2} \sum_{p,q} e^{-i\mathbf{k}_{pq} \cdot (\mathbf{r}_i^\parallel - \mathbf{r}_j^\parallel)} \left[\frac{k^2 \delta_{\nu\mu} - k_{pq\nu} k_{pq\mu}}{\kappa_{pq}} (\Delta_{pq}^+ + \tau \Delta_{pq}^-) + \eta \Sigma_{pq} \right] \\ & + \frac{1}{2} \sum_{n,m} \frac{e^{i\mathbf{k} \cdot \mathbf{s}_{nm}}}{T_{nm}^3} \{ \Gamma_{nm}^1 [\delta_{\nu\mu} \Gamma_{nm}^2 + (N_\nu + \nu)(N_\mu + \mu) \Gamma_{nm}^3] + \Gamma_{nm}^4 [-\delta_{\nu\mu} T_{nm} + (N_\nu + \nu)(N_\mu + \mu) \Gamma_{nm}^5] + \text{c.c.} \}, \end{aligned} \quad (\text{A15})$$

with

$$\nu, \mu = x, y, z;$$

$$\mathbf{N} = (n + \alpha m, \beta m, 0);$$

$$\eta = \begin{cases} 1 & \text{if } \nu = \mu = z \\ 0 & \text{otherwise;} \end{cases}$$

$$\tau = \begin{cases} -1 & \text{if } \nu = z \text{ or } \mu = z \\ +1 & \text{otherwise;} \end{cases}$$

$$T_{nm} = |\mathbf{N} + (\mathbf{r}_i - \mathbf{r}_j)|;$$

$$\begin{aligned} \Delta_{pq}^+ = & \Delta_{pq}(z_i - z_j) \\ = & e^{i\kappa_{pq}(z_i - z_j)} \operatorname{erfc} \left[-\frac{i\kappa_{pq}}{2E} - (z_i - z_j)E \right]; \end{aligned}$$

$$\Delta_{pq}^- = \Delta_{pq}(z_j - z_i);$$

$$\Sigma_{pq} = \frac{i4E}{\sqrt{\pi}} \exp \left[-(z_i - z_j)^2 E^2 + \frac{\kappa_{pq}^2}{4E^2} \right];$$

$$\Gamma_{nm}^1 = \exp(-ikT_{nm}) \operatorname{erfc} \left[T_{nm}E - \frac{ik}{2E} \right];$$

$$\Gamma_{nm}^2 = -1 - ikT_{nm} + k^2 T_{nm}^2;$$

$$\Gamma_{nm}^3 = -k^2 + \frac{3ik}{T_{nm}} + \frac{3}{T_{nm}^2};$$

$$\Gamma_{nm}^4 = \frac{2E}{\sqrt{\pi}} \exp \left[-E^2 T_{nm}^2 + \frac{k^2}{4E^2} \right];$$

$$\Gamma_{nm}^5 = \frac{3}{T_{nm}} + 2E^2 T_{nm};$$

and c.c. means "complex conjugate."

2. Intraplanar

For the calculation of the intraplanar transfer tensor the same procedure can be followed as for interplanar near. However, in this case $(\mathbf{r}_i - \mathbf{r}_j) = \mathbf{0}$, and we have to omit the interaction of the representing dipole with itself. This means that the interplanar lattice sum $S'(\mathbf{r}, \mathbf{k})$ can be written as

$$\begin{aligned} S'(\mathbf{r}, \mathbf{k}) = & S(\mathbf{r}, \mathbf{k}) - \frac{e^{ikr}}{r} \\ = & S^I(\mathbf{r}, \mathbf{k}) + S^{II}(\mathbf{r}, \mathbf{k}) \\ & - \frac{2}{\sqrt{\pi}} \int_{(0)}^E \exp \left[-r^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] d\epsilon \\ & - \frac{2}{\sqrt{\pi}} \int_E^\infty \exp \left[-r^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] d\epsilon, \end{aligned} \quad (\text{A16})$$

where we used (A2). Now the last integral of (A16) cancels with the $(n, m) = (0, 0)$ term in the sum S^{II} . So using the identity²⁹

$$\begin{aligned} & \frac{2}{\sqrt{\pi}} \int_{(0)}^E \exp \left[-r^2 \epsilon^2 + \frac{k^2}{4\epsilon^2} \right] d\epsilon \\ &= \frac{1}{2r} \left[e^{ikr} \operatorname{erfc} \left[rE + \frac{ik}{2E} \right] \right. \\ & \quad \left. - e^{-ikr} \operatorname{erfc} \left[rE - \frac{ik}{2E} \right] \right], \end{aligned} \quad (\text{A17})$$

we get

$$\begin{aligned} S'(\mathbf{r}, \mathbf{k}) &= S^I(\mathbf{r}, \mathbf{k}) + S^{II}(\mathbf{r}, \mathbf{k}) \\ &= -\frac{1}{2r} \left[e^{ikr} \operatorname{erfc} \left[rE + \frac{ik}{2E} \right] \right. \\ & \quad \left. - e^{-ikr} \operatorname{erfc} \left[rE - \frac{ik}{2E} \right] \right]. \end{aligned} \quad (\text{A18})$$

Inserting this into (A1) and evaluating it for $\mathbf{r} = \mathbf{0}$ we find

$$\begin{aligned} c^{\nu\mu}(\mathbf{k}) &= f_{ii}^{\nu\mu} + \left[\frac{2}{3} ik^3 \operatorname{erfc} \left[\frac{ik}{2E} \right] \right. \\ & \quad \left. + \frac{4E}{3\sqrt{\pi}} (k^2 - E^2) \exp \left[\frac{k^2}{4E^2} \right] \right] \delta_{\nu\mu}. \end{aligned} \quad (\text{A19})$$

It is easy to see that our expression for the intraplanar transfer tensor equals Litzman's, in the case $\alpha = 0$, $\beta = 1$.^{29,30} The components of $\vec{\epsilon}$ for the static case have been studied extensively in the past and yield the well-known lattice constants of dipole theory for square and hexagonal lattices.³¹ Approximate values of $\vec{\epsilon}$ have been obtained by Vlieger.³² We will include the self-interaction of the representing dipole in $\vec{\epsilon}$ in the form of the Lorentz radiation damping term $\frac{2}{3} ik^3$, a term which has to be added to the expression (A19).²⁹

APPENDIX B

It is quite straightforward to prove that the general expression for Eq. (15) gets the following form:

$$\begin{pmatrix} \vec{A}_1 & \cdots & \vec{B}_{1v} & \vec{B}_{1N_b} \\ \vdots & \ddots & & \\ \vec{B}_{v1} & & \vec{A}_v & \vec{B}_{vN_b} \\ & & & \ddots \\ \vec{B}_{N_b 1} & \vec{B}_{N_b v} & \cdots & \vec{A}_{N_b} \end{pmatrix} \begin{pmatrix} \mathbf{u}_{m1} \\ \vdots \\ \mathbf{u}_{mv} \\ \vdots \\ \mathbf{u}_{mN_b} \end{pmatrix} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad (\text{B1})$$

with

$$\vec{A}_v = (\vec{\alpha}_{Bv}^{-1} - \alpha_0 \vec{\epsilon}) + \sum_{p,q} \left[\frac{\vec{d}_{pq}}{1 - e^{-i(\kappa_{pq} - q_m)d_B}} + \frac{\vec{d}_{pq}}{1 - e^{-i(\kappa_{pq} + q_m)d_B}} \right], \quad (\text{B2a})$$

$$\begin{aligned} \vec{B}_{vw} &= -\vec{f}_{vw} + \sum_{p,q} \left[\frac{\vec{d}_{pq} e^{i\mathbf{k}_{pq} \cdot (\mathbf{r}_v^B - \mathbf{r}_w^B)}}{1 - e^{-i(\kappa_{pq} - q_m)d_B}} \right. \\ & \quad \left. + \frac{\vec{d}_{pq} e^{i\mathbf{k}_{pq} \cdot (\mathbf{r}_v^B - \mathbf{r}_w^B)}}{1 - e^{-i(\kappa_{pq} + q_m)d_B}} \right], \end{aligned} \quad (\text{B2b})$$

$$\vec{f}_{vw} = \begin{cases} \sum_{p,q} \vec{d}_{pq} e^{-i\mathbf{k}_{pq} \cdot (\mathbf{r}_v^B - \mathbf{r}_w^B)} & \text{if } v < w \\ \sum_{p,q} \vec{d}_{pq} e^{-i\mathbf{k}_{pq} \cdot (\mathbf{r}_v^B - \mathbf{r}_w^B)} & \text{if } v > w \end{cases} \quad (\text{B3a})$$

$$\vec{f}_{vw} = \begin{cases} \sum_{p,q} \vec{d}_{pq} e^{-i\mathbf{k}_{pq} \cdot (\mathbf{r}_v^B - \mathbf{r}_w^B)} & \text{if } v < w \\ \sum_{p,q} \vec{d}_{pq} e^{-i\mathbf{k}_{pq} \cdot (\mathbf{r}_v^B - \mathbf{r}_w^B)} & \text{if } v > w \end{cases} \quad (\text{B3b})$$

It is obtained by inserting (15) in (12) for every value of m . The rows of Eq. (B1) represent a system of simultaneous linear equations. We show now that if the equation given by the first row of (B1) is fulfilled, the commensurability theorem (10) causes the equations given by all other rows of (B1) to be fulfilled. Using (10) with $\mathbf{u}_m = \mathbf{u}_{m1}$, we can write

$$(\vec{A}_1 + \cdots + \vec{B}_{1v} e^{i\mathbf{k}_m \cdot \mathbf{r}_v} + \cdots + \vec{B}_{1N_b} e^{i\mathbf{k}_m \cdot \mathbf{r}_{N_b}}) \mathbf{u}_m = 0, \quad (\text{B4a})$$

$$\begin{aligned} & (\vec{B}_{v1} e^{i\mathbf{k}_m \cdot (-\mathbf{r}_v)} + \cdots + \vec{A}_v \\ & \quad + \cdots + \vec{B}_{vN_b} e^{i\mathbf{k}_m \cdot (\mathbf{r}_{N_b} - \mathbf{r}_v)}) \mathbf{u}_m = 0, \end{aligned} \quad (\text{B4b})$$

with arbitrary v . Now if (B4a) is fulfilled, if we use (10) and if $\vec{\alpha}_{B1} = \vec{\alpha}_{Bv}$ (i.e., we are dealing with the same types of dipoles), then $\vec{A}_1 = \vec{A}_v$ and (B4b) is fulfilled if

$$\begin{aligned} \sum_{w=2}^{N_b} \vec{B}_{1w} e^{i\mathbf{k}_m \cdot \mathbf{r}_w^B} &= \sum_{w=1}^{v-1} \vec{B}_{vw} e^{i\mathbf{k}_m \cdot (\mathbf{r}_w^B - \mathbf{r}_v^B)} \\ & \quad + \sum_{w=v+1}^{N_b} \vec{B}_{vw} e^{i\mathbf{k}_m \cdot (\mathbf{r}_w^B - \mathbf{r}_v^B)}. \end{aligned} \quad (\text{B5})$$

Inserting the expression (B4b) into (B5) we get the following identity to hold:

$$\begin{aligned}
& \sum_{p,q} \left[\frac{\vec{d}_{pq}}{1 - e^{-i(\kappa_{pq} - q_m)d_B}} \right] \left[\sum_{w=2}^{N_B} e^{i(\kappa_{pq} - q_m)(-z_w)} - \sum_{w=1}^{v-1} e^{i(\kappa_{pq} - q_m)(z_v - z_w - d_B)} - \sum_{w=v+1}^{N_B} e^{i(\kappa_{pq} - q_m)(z_v - z_w)} \right] \\
&= \sum_{p,q} \left[\frac{\vec{d}_{pq}}{1 - e^{-i(\kappa_{pq} + q_m)d_B}} \right] \left[\sum_{w=2}^{N_B} e^{-i(\kappa_{pq} + q_m)(-z_w + d_B)} - \sum_{w=1}^{v-1} e^{-i(\kappa_{pq} + q_m)(z_v - z_w)} - \sum_{w=v+1}^{N_B} e^{-i(\kappa_{pq} + q_m)(z_v - z_w + d_B)} \right].
\end{aligned} \tag{B6}$$

This can only be true if both the expressions between the second sets of large parentheses on both the left and right are zero. They both, however, yield the same condition, namely

$$z_v = \frac{v-1}{N_B} d_B. \tag{B7}$$

This means that the representing dipoles in the bulk unit cell have to be distributed in a regular way as far as their z component is concerned: for $N_B = 2$ we have $z_1 = 0$, $z_2 = d_B/2$; for $N_B = 3$, $z_1 = 0$, $z_2 = d_B/3$, $z_3 = 2d_B/3$; and so forth.

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