A discrete theory of the induced polarization of adsorbed atoms and molecules on an ionic crystal

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Abstract

The potential response of a non-planar dielectric crystal surface to a fluctuating electronic charge density of admolecules is characterized using a discrete approach and quasi-static approximation. In this method, the multipolar response function of the ionic crystal is introduced from a general propagator of potential and the electric properties of the adsorbed molecules are described as the electric susceptibility. This allows us to obtain an iterative self-consistent determination of the long-range van der Waals interaction potential. The discrete description of the crystal matter takes into account the influence of the face specificity and adsorption sites of the substrate. The multipolar (electrostatic + induction) contribution and the quantum (dispersion) terms are determined for the dipolar and the quadrupolar moments of the molecule. A numerical application of each contribution is given for a xenon atom adsorbed on an MgO surface.

1. Introduction

When a molecule (or an atom) is located in the vicinity of a solid body it gives rise to a permanent electric polarization. This permanent electric polarization is due to the deformation of the charge distribution which results from the influence of the dispersive, inductive and electrostatic long-range interactions between the two bodies.

Collision-induced spectroscopy in the far-IR and microwave range manifests this induced polarization [1], and, as is well known, the change in work function due to the adsorption of atoms on a metal surface is attributed to the net dipole acquired by the atom–surface system [2]. Moreover, on another scale involving nanometer size structures, new local probe methods (*e.g.* near field microscopy) have shown that polarization induced in the probe plays a dominant role in the prediction of images of corrugated surfaces [3, 4]. The quantitative prediction of these physical effects is important for interpreting such phenomena.

Several theoretical approaches to determination of the permanent electric polarization for adatoms have been developed on the basis of a dynamic treatment with continuous description of the substrate [5, 6], and have shown that the magnitude of the induced dipole moment varies as d^{-4}, where d is the atom–surface distance.

The polarization induced for molecules adsorbed on a solid body has been less investigated. The first contribution on this subject was that of Linder and Kromhout [7], who calculated the induced dipole of an arbitrary molecule interacting with an arbitrary system described as a continuum medium of dielectric constant $\varepsilon(\omega)$ limited by a perfect planar surface.

Nevertheless, although these models represent appreciable improvements in the quantitative understanding of this mechanism, they all neglect the discrete nature of the matter and, more particularly, they disregard possible adsorption site and face-specific effects. Indeed, recent experimental studies of the adsorption of a xenon monolayer on the (100), (110) and (111) surfaces of palladium have shown an increase in magnitude of the induced dipole of the xenon atom physisorbed successively on the (110), (100) and (111) faces of palladium metal [8]. In this paper, we present an alternative method for calculating the van der Waals moments of the adsorbed molecule on a solid surface, taking into account the discrete nature of the matter.

This model allows us to explain the adsorption site effect which takes into account the dispersion, induction, and electrostatic long-range interaction. The general propagator of the potential is calculated using a new method which recognizes the discrete nature of the substrate where the correlation between the atomic sites is neglected.

In Section 2 we present the determination of the dipolar and quadrupolar moments in the admolecule. Detailed expressions used to describe the substrate are given in Section 3. Section 4 is devoted to the application of a xenon atom adsorbed on the (100) face of an MgO surface.

2. The permanent induced multipolar moments of the admolecule

When a molecule is placed near a solid, its initial charge distribution $\rho_0(r, \omega)$ is modified by the van der Waals interaction between the two bodies. A permanent induced multipolar moment of nth order $M^{(n)}(r_0, \omega)$ of the adsorbate molecule is produced

$$M^{(n)}(r_0, \omega) = M_e^{(n)}(r_0, \omega) + M_i^{(n)}(r_0, \omega) + M_d^{(n)}(r_0, \omega)$$

(1)

This induced moment $M^{(n)}$ (r_0, ω) may be connected to the charge density by

$$\rho(r, \omega) = \sum_n \frac{(-1)^n}{(2n-1)!!} M^{(n)}(r_0, \omega)[n] \nabla_r^{(n)} \delta(r - r_0)$$

(2)

where ∇_r is the gradient operator of nth order. In eqn. (1), the two first classical terms, $M_e^{(n)}(r_0, \omega)$ and $M_i^{(n)}(r_0, \omega)$, correspond respectively to the electrostatic effect due to the local electric potential $\phi_1(r)$ generated by the charges present in the ionic substrate and the modification induced by the potential image of the initial charge density $\rho_0(r)$ of the isolated molecule in the substrate.

In the linear response theory, the electrostatic and inductive modification of the charge density of the molecule may be obtained by a series expansion in terms of the local potential $\phi_1(r)$, linear susceptibilities $^\rho\chi^\rho(r, r_1, \omega)$ of the molecule and of the potential propagator operator $K(r, r_1, \omega)$ of the solid

$$\rho_e(r, \omega) = \int {}^\rho\chi^\rho(r, r_1, \omega)\phi(r_1) \, dr_1$$

(3)

and

$$\rho_i(r, \omega) = \iint {}^\rho\chi^\rho(r, r_1, \omega)K(r_1, r_2, \omega)\rho_0(r_2) \, dr_1 \, dr_2$$

$$+ \iiint {}^\rho\chi^\rho(r, r_1, \omega)K(r_1, r_2, \omega)$$

$$\times {}^\rho\chi^\rho(r_2, r_3, \omega)\phi_1(r_3) \, dr_1 \, dr_2 \, dr_3$$

(4)

The last quantum term $M_d^{(n)}(r_0, \omega)$ in eqn. (1) corresponds to a dispersive effect which is due to the correlations between the charge density fluctuations in the system (molecule + solid). It is shown in ref. 9 that the dispersive modification charge density $\rho_d(r, \omega)$ may be

expressed in terms of the non-linear response function $^\rho\chi^{\rho+\rho}(r, r_1, r_2, \omega_1, \omega_2)$ of the adsorbed molecule.

$$\rho_d(r, \omega) = -\frac{\hbar}{2\pi} \int_0^{+\infty} d\xi \iint {}^\rho\chi^{\rho+\rho}(r, r_1, r_2, i\xi, 0)$$

$$\times K(r_1, r_2, i\xi) \, dr_1 \, dr_2$$

(5)

For the weak extended molecule, we neglect in the following contributions of higher order than quadrupolar. After the substitution of eqn. (2) into eqns. (3), (4) and (5), and straightforward calculation, one finally obtains compact expressions of the electrostatic, inductive and dispersive contributions for the induced dipole $\mu(r_0, \omega) = M^{(1)}(r_0, \omega)$ and quadrupole $\theta(r_0, \omega) = M^{(2)}(r_0, \omega)$. We give these contributions in ref. 10 expressed in terms of the electric field $E_1(r)$ and of its gradient $F_1(r)$ corresponding to the local potential $\phi_1(r)$ and in terms of the multipolar propagator $^{(m)}S^{(n)}(r, r_1, \omega)$ of the successive field gradients generated by the surface and defined with the general propagator $K(r, r_1, \omega)$ of the potential by:

$${}^{(m)}S^{(n)}(r, r_0, \omega) = [\nabla_r^{(m)}\nabla_r^{(n)}K(r, r_1, \omega)]_{r=r_1=r_0}$$

(6)

where r_0 denotes the position vector of the center of mass of the molecule.

3. A microscopic discrete approach for the solid

The substrate properties may be described using the general propagator $K(r, r_1, \omega)$ of the potential and the local potential $\phi_1(r)$. We present here a new method to determine $K(r, r_1, \omega)$. In the particular case, the MgO solid crystallizes in a cubic close packed structure with two atoms Mg and O per unit cell. Using the microscopic discrete model presented in ref. 11 in which we neglected the correlation between the various atomic sites of the substrate and the contributions of higher order than dipolar of each site, leads to

$${}^{(m)}S^{(n)}(r, r_0, \omega) = \sum_i \alpha_s(\omega){}^{(m)}T^{(1)}(r, R_i)^{(1)}T^{(n)}(R_i, r_0)$$

(7)

where the index i denotes the ith order of the site and $^{(m)}T^{(n)}(r, R_i)$ is the multipolar propagator of the field in the vacuum. In the quasistatic asymptotic case this $(m+n)$th rank tensor has a very simple form:

$${}^{(m)}T^{(n)}(r, R_i) = \frac{(-1)^n}{(2n-1)!!} \nabla_r^{(m)}\nabla_R^{(m)}\left[\frac{1}{|r - R_i|}\right]$$

(8)

After the substitutions of eqns. (7) and (8) into eqn. (6), and straightforward calculations, one obtains the same expression for the general propagator $K(r, r_0, \omega)$ of the potential as that determined in ref. 12:

$$K(r, r_0, \omega) = \frac{1}{S} \sum_{s,p} \sum_g \exp(i g \cdot \tau_{sp}) \int \frac{dk}{k|k+g|}$$

$$\times K \cdot \alpha_s(\omega) \cdot K_g^* \exp\{-i[k \cdot l - (k+g) \cdot l']\}$$

$$\times \exp[k(z - z_p) + |k+g|(z' - z_p)] \qquad (9)$$

The vector k is defined by its components $k = (k_x, k_y)$ and its modulus k. S and g represent the area of the unit cell and the reciprocal lattice vector $(2\pi/a)(g_1 x + g_2 y)$ respectively. We also define the position $r = (l, z)$ and the relative position vector τ_{sp} of the atoms of the substrate in a given cell and in two different planes p. We may also write the expression of the local potential $\phi_1(r)$ in the reciprocal planar lattice [12]:

$$\phi_1(r) = \frac{2\pi}{S} \sum_{s,p} \sum_g \frac{L_p q_s}{g} \exp[-g(z - z_p) + i g \cdot (l - \tau_{sp})]$$

$$(10)$$

where L_p and q_s respectively denote the screening factor and the sth atom charge of the primitive cell. We introduce the continuum $(g \equiv 0)$ and corrugated $(g \neq 0)$ characters of the substrate matter in the expression of the propagator $K(r, r_0, \omega)$.

$$\bar{K}(r, r_0, \omega) = \frac{2}{S} \sum_{s,p} \alpha_s(\omega) \int dk \exp[ik' \cdot (l' - l)]$$

$$\times \exp[-k(z - z_p)] \exp[-k'(z' - z_p)] \qquad (11)$$

and

$$\tilde{K}(r, r_0, \omega) = \frac{2}{S} \sum_{g_1 > 0} \sum_{g_2 \neq 0} \sum_{s,p} \alpha_s(\omega) \int dk \, \Pi(k, g, z, z')$$

$$\times \cos(l' \cdot k_g - l \cdot k - g \cdot \tau_{sp}) \qquad (12)$$

with

$$\Pi(k, g, z, z') = \left(\frac{k \cdot g + k^2 + k k_g}{k k_g} \right)$$

$$\times \exp[-k(z - z_p)] \exp[-k_g(z' - z_p)]$$

$$(13)$$

Equations (12) and (13) take into account the discrete description of the ionic crystal.

4. Application to adsorbate atoms on an MgO crystal

When the molecule is reduced to an atom, the non-vanishing contributions for the induced dipole and quadrupole moments are

$$\mu_e(r_0, \omega) = {}^1\alpha^1(\omega) \cdot E_1(r_0) \qquad (14)$$

$$\mu_d(r_0, \omega) = -\frac{\hbar}{6\pi} \int_0^{+\infty} [{}^1\chi^{1+2}(i\xi, 0) : {}^{(1)}S^{(2)}(r_0, r_0, i\xi)$$

$$+ {}^1\chi^{2+1}(i\xi, 0) : {}^{(2)}S^{(1)}(r_0, r_0, i\xi)] \, d\xi \qquad (15)$$

and

$$\theta_e(r_0, \omega) = \frac{1}{3} {}^2\alpha^2(\omega) : F_1(r_0) \qquad (16)$$

$$\theta_d(r_0, \omega) = -\frac{\hbar}{2\pi} \int_0^{+\infty} {}^2\chi^{1+1}(i\xi, 0) : {}^{(1)}S^{(1)}(r_0, r_0, i\xi) \, d\xi$$

$$(17)$$

For the numerical calculation, we evaluate the hyperpolarizabilities ${}^1\chi^{1+2}(\omega, 0)$ and ${}^2\chi^{1+1}(\omega, 0)$ of the adatom as an isotropic three-dimensional harmonic oscillator with frequency ω_a:

$${}^1\chi^{1+2}(\omega, 0) \equiv {}^2\chi^{1+1}(\omega, 0) \equiv {}^1\chi^{2+1}(\omega, 0)$$

$$= {}^1\chi^{1+2}(0, 0) \frac{\omega_a^2}{\omega_a^2 - \omega^2} \qquad (18)$$

with

$${}^1\chi^{1+2}(0, 0) = -\frac{2\eta}{\hbar \omega_a} \qquad (19)$$

where η is the parameter calculated by Byers Brown and Whisnant [13].

We also introduce the strength coefficient $C_6(s)$ between the physisorbed atom and cations Mg^{2+} $(s = 1)$ and the atom and anions O^{2-} $(s = 2)$:

$$C_6(s) = \frac{3\hbar}{\pi} \int_0^{+\infty} \alpha_s(i\xi)\alpha(i\xi) \, d\xi \qquad (20)$$

The parameter $C_6(s)$ of the various pairs (atom, ion) are obtained from refs. 14–16. In Table 1 we list all the parameters of the system (atom + solid) used to calculate the induced dipole and quadrupole moments of the physisorbed xenon atom on the (100) face of MgO. Use of eqns. (6), (9), ..., (20), leads to

$$\mu_e(r_0) = \frac{4\pi\alpha}{S} \sum_{s,p} \sum_{g_1 > 0} \sum_{g_2 \neq 0} L_p q_s \exp[-g(d + pb)]f(l_M)$$

$$(21)$$

$$\theta_e(r_0) = -\frac{8\pi^2 \alpha^{(2)}}{3S} \sum_{s,p} \sum_{g_1 > 0} \sum_{g_2 \neq 0}$$

$$\times L_p q_s \exp[-g(d + pb)]f(l_M) \qquad (22)$$

and

$$\bar{\mu}_d(r_0) = \frac{2\eta\pi}{3S} \sum_{s,p} \frac{C_6(s)}{(d + pb)^5} \qquad (23)$$

TABLE 1. The system (Xe–MgO) parameters in atomic units (a.u.)

Xenon parameter	$C_6(s=1)^a$	$C_6(s=2)^a$	η	ω_a	α	$^2\alpha^2$
Value	27.95	166.04	150[b]	0.535	27.11	110.4
MgO parameter	τ_1	τ_2	a	b	q_1/e	q_2/e
Value	(0, 0)	(2.81, 2.81)	5.63	3.93	1.99^c	-1.99

[a]Calculated values [16].
[b]Estimated value [6].
[c]e is the elementary charge [17].

$$\bar{\theta}_d(r_0) = \frac{\eta\pi}{\hbar\omega_a\alpha S} \sum_{s,p} \frac{C_6(s)}{(d+pb)^4} \tag{24}$$

$$\tilde{\mu}_d(r_0) = \frac{2\eta\pi}{\hbar\omega_a\alpha S} \sum_{s,p} \sum_{g_1>0} \sum_{g_2\neq0}$$
$$\times \frac{C_6(s)g^3}{(d+pb)^2} K_3(g(d+pb))f(l_M) \tag{25}$$

$$\tilde{\theta}_d(r_0) = \frac{2\eta\pi}{3\hbar\omega_a S} \sum_{s,p} \sum_{g_1>0} \sum_{g_2\neq0} C_6(s)W(g,d)f(l_M) \tag{26}$$

The parameter b corresponds to the distance between two consecutive planes parallel to the surface and $f(l_M) = \cos[g \cdot (l_M - \tau_{sp})]$. The function $W(g, d)$ may be defined by:

$$W(g,d) = \int dk \frac{(k \cdot g + k^2 + kkg)(kkg - 1/2k \cdot kg)}{kkg}$$
$$\times \exp[-(k+kg)(d+pb)] \tag{27}$$

Using the values given in Table 1 it is possible to evaluate the different contributions, eqns. (21)–(26), for the dipole and quadrupole moments of a xenon atom adsorbed at the equilibrium distance $d = 3.2$ Å on four particular sites defined in Fig. 1. Some remarks can be made about this process (see Table 2).

(1). The magnitude of the total induced dipole moment $(\mu_e + \mu_i + \mu_d)$ of a xenon adsorbed on site 2 can be estimated to about 0.3 debye. The non-negligible dipolar contribution $V_{\mu\mu}$ of the induced polarization can describe the mediated energy of an adsorbed monolayer. Indeed, for a (2×2) overlayer structure of xenon [16] in which each atom occupies site 2, one finds that $V_{\mu\mu} \approx 10$ mV per adsorbed atom.

(2) When one goes from an oxygen site to a magnesium site, the electrostatic dipole moment varies from $+0.18$ to -0.18 debye. Such a contribution is very sensitive to the corrugation of the surface and then to the adsorption site.

(3) The influence of the corrugation of the surface on the dispersive induced dipole moment is smaller and contributes to the total magnitude by 20% only. This result is close to that obtained for the corrugation energy with respect to its continuum part.
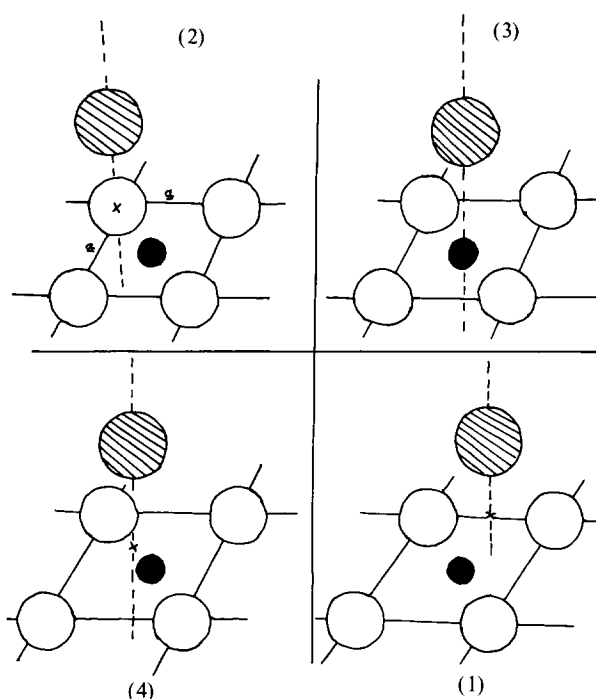

Fig. 1. Xenon atom physisorbed on the four adsorption sites of MgO which are defined as (1), (2), (3) and (4): ○ oxygen atoms; ● magnesium atom; ◉ xenon atom.

TABLE 2. Dipolar and quadrupolar contributions (in debye units) for a xenon atom adsorbed on four sites of a (100) face of an MgO crystal

Site	μ_e	$\bar{\mu}_d$	$\tilde{\mu}_d$	θ_e	$\bar{\theta}_d$	$\tilde{\theta}_d$
(1)	0.000	0.125	0.003	0.000	0.139	−0.004
(2)	0.172	0.125	−0.013	−0.290	0.139	−0.017
(3)	−0.172	0.125	0.019	0.290	0.139	0.021
(4)	0.000	0.125	−0.002	0.001	0.139	−0.003

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