LBL-16006 c.2
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY
JUL 5 1983
LIBRARY AND
DOCUMENTS SECTION

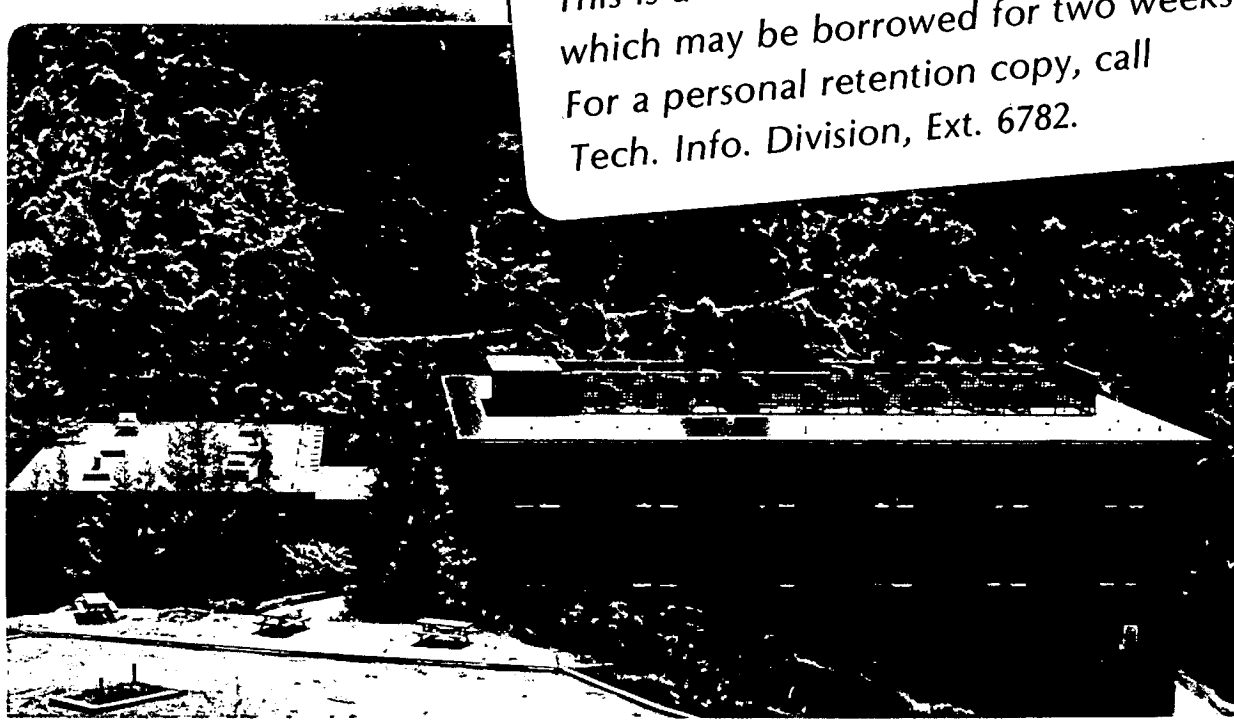
Submitted to Physical Review B

LOCAL FIELD EFFECT ON LINEAR AND NONLINEAR OPTICAL PROPERTIES OF ADSORBED MOLECULES

P. Ye and Y.R. Shen

May 1983

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



LBL-16006 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Physical Review B
PACS 68.45-v, 42.65cq, 07.60-j

LBL-16006

LOCAL FIELD EFFECT ON LINEAR AND NONLINEAR OPTICAL PROPERTIES OF ADSORBED MOLECULES*

Peixian Ye and Y. R. Shen

Department of Physics
University of California
Berkeley, California 94720

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

ABSTRACT

A classical point dipole model is used to calculate the local field effect on the optical properties of adsorbed molecules on a substrate. The spatially non-varying component of the local field at the molecules can be described by using a local-field correction factor. Equally important is the spatially varying component of the local field which arises mainly from the molecule - substrate interaction. The rapid variation over the molecular dimension can appreciably modify the transition matrix elements and break down the electric dipole selection rules. The effect becomes insignificant if the molecules are more than 2.5 Å away from the substrate even in the metal case. Both components of the local field contribute to the effective linear and nonlinear polarizabilities of the adsorbed molecules. Nonlinearity due to molecular response to the harmonic

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

I. INTRODUCTION

The potential of nonlinear optical techniques for surface studies has recently been recognized.[1] Initial attempts in this area has proven to be very successful. The second-order nonlinear processes, in particular, appear most attractive because of their experimental simplicity and their relatively high surface sensitivity.[2] By symmetry, such processes are forbidden in media with an inversion center, but they are allowed on surfaces or interfaces. This surface-specific nature makes the second-order nonlinear optical processes most appropriate for probing of molecules adsorbed at an interface between two centrosymmetric media.

The lack of inversion symmetry of an adsorbed molecular monolayer results from two possible causes. First, the molecules themselves may have no inversion symmetry. Their alignment on the surface through adsorption forms a molecular layer with no inversion center. Second, even if the molecules are centrosymmetric, the molecule-substrate interaction can effectively break the symmetry. We shall call the interaction, in the absence of any applied field, the "chemical" interaction. This interaction modifies the eigenenergies and eigenfunctions of the adsorbed molecules, and therefore, changes the properties of the molecules. Then, in the presence of an applied field, there also exist the induced dipole-induced dipole interaction between molecules and induced dipole-image dipole interaction between the molecules and the substrate. We shall call these field-induced interactions the "electromagnetic" interaction. It results in the creation of a local field at the molecules different from the applied field, and hence, an effective polarizability for the molecules different from the real one. In this paper, we shall only be concerned

with the electromagnetic interaction.

The quantum theory of local field is admittedly very difficult, especially when the eigenstates of the adsorbed molecules and the substrate are not known.[3] There, however, exists the classical local-field theory based on the point-dipole model.[4] Bagchi et al.[5] has recently used such a theory to calculate the effective linear optical polarizability of molecules adsorbed on a substrate. As in the bulk, a local-field correction factor is adopted to describe the average local field at the molecules. It depends on the molecular polarizability, the distances between molecules and between the molecules and the substrate, and the dielectric constant of the substrate.

In calculating the effective nonlinear polarizability of the adsorbed molecules, the same local-field correction factor should also appear in conjunction with each field component.[6] In addition, the electromagnetic interaction also breaks the inversion symmetry of a centrosymmetric molecule sitting on a substrate? Using the point-dipole model, Antoniewicz[7] has shown that the second-order nonlinearity of an adsorbed molecule can indeed arise from the induced dipole-image dipole interaction. Assume an incoming field at ω induces an oscillating dipole on an adsorbed molecule. The induced dipole-substrate interaction can then be described by the induced dipole-image dipole interaction. Since it is only the electron cloud in the molecule actually responding to the optical field, both the induced dipole and the image dipole should have their centers vibrating in space at the frequency ω. Consequently, the local field at the molecule created by the oscillating image dipole should have a harmonic component at 2ω. This results in a 2ω component in the dipole oscillation,

and leads to the second-harmonic generation from the adsorbed molecule. The same picture can be extended to yield a local field with all the harmonic components. Using this model, Antoniewicz proposed to explain the observed second-harmonic generation from centrosymmetric molecules adsorbed on silver.[8] A similar model was previously used to explain the surface enhanced Raman scattering.[9] In both cases, however, a rather small distance between the molecules and the substrate was chosen in order to yield the observed signal strength, indicating that other mechanisms are probably more important.

The above model of Antoniewicz should be expected to fall naturally from a local-field theory that properly takes into account all the dipole interactions. Aside from the harmonic components, the local field should also have a strong spatial variation along the surface normal. If the local field varies significantly across a molecule, then the induced polarization on the molecule should result not only from the dipole contribution, but also from the higher-order multipole contributions.[6,10] Actually, the multipole expansion may not even be appropriate in this case, considering the very rapid spatial variation of the field. An immediate consequence of this is that the transition matrix elements are now different from the dipole matrix elements. Accordingly, both the linear and nonlinear polarizabilities of the molecules are modified, and the parity selection rules broken. Such a mechanism is clearly more important for molecules with more extended wavefunctions.

The main objective of this paper is to formulate the local field picture outlined above for of the effect of the electromagnetic interaction on the second-order nonlinearity of adsorbed molecules.

We use the classical theory and the point-dipole model to describe the local field arising from the induced dipole-induced dipole interaction and the induced dipole-image dipole interaction. The local field, shown explicitly with its spatial dependence and the harmonic components, is then used in the semi-classical theory to calculate the induced polarization (or the effective dipole) on the adsorbed molecules. It will be seen that in addition to the local field correction factor, the local field with its strong spatial variation can also change the polarizabilities of the molecules significantly. It will also be shown that the second-order nonlinearity of the adsorbed molecules is most likely dominated by the nonlinear response of the molecules to the fundamental component of the local field rather than the linear response to the harmonic or mixed frequency component of the local field.

In Sec. II, the point-dipole model used to calculate the local field at the adsorbed molecules is reviewed, and an expression for the spatially varying local field with its harmonic frequency components is obtained. The local field is then used in Sec. III to derive the effective linear and second-order nonlinear polarizabilities of the adsorbed molecules. Finally, Sec. IV is devoted to general analysis and discussion from which we gain some insight into the extent the linear and nonlinear optical properties of the adsorbed molecules is affected by the electromagnetic interaction.

II. LOCAL FIELD AT ADSORBATES

Following Bagchi et al.,[5] we assume a monolayer system of adsorbed molecules forming a two-dimensional square lattice on a substrate with a

lattice constant "a". The substrate which occupies the semi-infinite space of $z \geqslant 0$ is characterized by a dielectric constant ε. In an applied field, a dipole is induced on each adsorbed molecule. The centers of the dipoles are taken as $\vec{R}_{ij} = (ia, ja, -Z_o)$ where i and j are integers, and Z_o is the distance of the molecules from the substrate. We also assume that the molecules are axially symmetric, with the molecular axis perpendicular to the surface of the substrate. The linear polarizability of the molecules is then a tensor with only the diagonal elements $\alpha_{xx} = \alpha_{yy}$ and α_{zz}.

The point-dipole model together with the image-dipole approach is now used to calculate the local field at the molecules. The dipoles induced on the molecules at $\vec{R}_{ij}$ by an applied field $\vec{E}(\omega)$ are

$$\vec{\mu}(\omega) = \overleftrightarrow{\alpha}(\omega) \cdot \vec{E}_{\ell oc}(\omega) \tag{1}$$

where $\vec{E}_{\ell oc}(\omega) \cong \overleftrightarrow{L}(\omega) \cdot \vec{E}(\omega)$ and $\overleftrightarrow{L}(\omega)$ is the local field correction factor. The image dipoles appear at $\vec{R}'_{ij} = (ia, ja, Z_o)$ and have the expression[5]

$$\vec{\mu}_I(\omega) = \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} [-\mu_x\hat{x} - \mu_y\hat{y} + \mu_z\hat{z}]. \tag{2}$$

The local field is the sum of the applied field and the dipole field. Let $\vec{r}$ be the position of a local point in a molecule with reference to the center of the molecule. We choose the molecule at $\vec{R}_{oo} = 0$ as the representative one. Then, the local field at $\vec{r}$ is given by

$$\vec{E}_{\ell oc}(\vec{r}) = \vec{E} + \vec{E}_{dip}(\vec{r}) + \vec{E}_{dip,I}(\vec{r}). \tag{3}$$

Here, $\vec{E}_{dip}(\vec{r})$ is the field at $\vec{r}$ created by all the induced dipoles on the adsorbed molecules except the one at which $\vec{r}$ is located.

$$\vec{E}_{dip}(\vec{r}) = \sum_{i,j=-\infty}^{\infty} \frac{3[\vec{\mu} \cdot (\vec{R}_{ij} - \vec{r})](\vec{R}_{ij} - \vec{r}) - \vec{\mu}(\vec{R}_{ij} - \vec{r})^2}{(\vec{R}_{ij} - \vec{r})^5} . \quad (4)$$

$\vec{E}_{dip,I}(\vec{r})$ is the field at $\vec{r}$ created by all the image dipoles.

$$\vec{E}_{dip,I}(\vec{r}) = \sum_{i,j=-\infty}^{\infty} \frac{3[\vec{\mu}_I \cdot (\vec{R}'_{ij} - \vec{r})](\vec{R}'_{ij} - \vec{r}) - \vec{\mu}_I(\vec{R}'_{ij} - \vec{r})^2}{(\vec{R}'_{ij} - \vec{r})^5} . \quad (5)$$

It is easily seen that $|\vec{E}_{dip}(\vec{r})|$ is centrosymmetric with respect to the center of a molecule, but $|\vec{E}_{dip,I}(\vec{r})|$ is not in the $\hat{z}$-direction. The sums in Eqs. (4) and (5) with $\vec{r} = 0$ have already been calculated by Bagchi et al.[5] The result yields

$$\vec{E}_{\ell oc}(\vec{r} = 0) = \overleftrightarrow{L}(\omega) \cdot \vec{E}(\omega) \quad (6)$$

with the local field correction factor given by

$$L_{xx}(\omega) = L_{yy}(\omega) = \left\{1 + \frac{\alpha_{xx}(\omega)}{2a^3}[\xi_o - \rho(\omega)\xi_I]\right\}^{-1}$$

$$L_{zz}(\omega) = \left\{1 - \frac{\alpha_{zz}(\omega)}{a^3}[\xi_o + \rho(\omega)\xi_I]\right\}^{-1} \quad (7)$$

where

$$\xi_o = -9.0336$$

cont'd

$$\xi_I = 16\pi^2 \sum_{i=0}^{\infty} \sum_{j=1}^{\infty} (i^2 + j^2)^{\frac{1}{2}} \exp\left[- \frac{4\pi Z_o}{a} (i^2 + j^2)^{\frac{1}{2}}\right]$$

$$\rho(\omega) = [\varepsilon(\omega) - 1]/[\varepsilon(\omega) + 1].$$

The gradient of the local field at $\vec{r} = 0$ can also be calculated. We find, with $\nabla\vec{E}$ neglected,

$$\nabla_x E_{\ell oc,y} = \nabla_y E_{\ell oc,x} = 0$$

$$\nabla_x E_{\ell oc,x} = \nabla_y E_{\ell oc,y} = - 2\nabla_z E_{\ell oc,z} = - \rho(\omega) \frac{2\mu_z(\omega)}{a^3} \xi_I M$$

$$\nabla_z E_{\ell oc,x} = \nabla_x E_{\ell oc,z} = \rho(\omega) \frac{\mu_x(\omega)}{2a^3} \xi_I M$$

$$\nabla_z E_{\ell oc,y} = \nabla_y E_{\ell oc,z} = \rho(\omega) \frac{\mu_y(\omega)}{2a^3} \xi_I M \tag{8}$$

where

$$M = \frac{2\pi}{a} \frac{\sum_{i=0}^{\infty} \sum_{j=1}^{\infty} (i^2 + j^2) e^{-\frac{4\pi Z_o}{a} (i^2+j^2)^{\frac{1}{2}}}}{\sum_{i=0}^{\infty} \sum_{j=1}^{\infty} (i^2 + j^2)^{\frac{1}{2}} e^{-\frac{4\pi Z_o}{a} (i^2+j^2)^{\frac{1}{2}}}} .$$

To see the importance of the local field correction, we show in Fig. 1 an example of how L_{xx} and L_{zz} vary with Z_o. We assume a = 5 Å, $\varepsilon(\omega) = 10$, $\alpha_{xx}(\omega) = 6$ Å^3, and $\alpha_{zz}(\omega) = 11$ Å. While $L_{xx} = L_{yy}$ is always larger than 1, L_{zz} can be larger or smaller than 1, depending on how Z_o compares with a. This is fairly easy to understand from the dipole field

pattern. In the $\hat{x}$ direction, the dipole field from μ_x and $\mu_{I,x}$ always adds to the incoming E_x field. In the $\hat{z}$ direction, the dipole field from $\mu_{I,z}$ also adds to E_z, but that from μ_z is opposite to E_z. We should note that unlike the bulk case, where the local field correction factor is usually defined as the correction on the average macroscopic field in a medium, the local field correction factor here is defined with respect to the applied field outside a medium. Consequently, L_{xx}, L_{yy} and L_{zz} in the present case are much closer to 1 than the usual local field correction factor in a bulk condensed matter.

Because of the intrinsic asymmetry of the surface, the spatial variation of the local field at the molecules can be quite strong if $Z_o \lesssim a$. It is mainly due to the field created by the image dipoles. An example with $Z_o = \frac{1}{3}a = 1.7$ Å and $\varepsilon(\omega) = 10$ is shown in Fig. 2. The curve of $E_{\ell oc,z}$ versus z exhibits an appreciable variation in a region comparable to the size of a molecule. In fact, the variation is so strong that it cannot even be approximated by a linear function. Such a strong variation of the field over the dimension of a molecule will certainly affect the polarizabilities of the molecule since the electric dipole approximation is no longer valid in the semi-classical derivation of the polarizabilities. Even the multipole expansion is not really appropriate in this case. We shall discuss the derivation of the polizabilities at length in the next section.

In the above discussion of local field, we have assumed that the centers of the dipoles remain unchanged. More realistically, however, the centers of the oscillating dipoles also oscillate in space with respect to their equilibrium positions. Let $\{\vec{S}_{ij}(t)\}$ be the time-varying centers of the induced dipoles and image dipoles. Then, the local field at $\vec{r}$ created by the

dipoles at $\{\vec{S}_{ij}(t)\}$ instead of at $\{\vec{R}_{ij}\}$ can be calculated from Eqs. (3-5) with $\{\vec{R}_{ij}\}$ replaced by $\{\vec{S}_{ij}(t)\}$. We notice that since the dipoles are in phase, we have

$$\vec{E}_{dip}(\vec{r}\ ,\ \{\vec{S}_{ij}\}) - \vec{E}_{dip}(\vec{r} - \vec{S}_{oo},\ \{\vec{R}_{ij}\})$$

$$\vec{E}_{dip,I}(\vec{r}\ ,\ \{\vec{S}_{ij}\}) = \vec{E}_{dip,I}[\vec{r} - \hat{x}(S_{oo})_x - \hat{y}(S_{oo})_y + \hat{z}(S_{oo})_z,\ \{\vec{R}_{ij}\}].$$

Therefore, by Taylor's series expansion, we find

$$\vec{E}_{\ell oc}(\vec{r}\ ,\ \{\vec{S}_{ij}\}) = \vec{E}_{\ell oc}(\vec{r}\ ,\ \{\vec{R}_{ij}\}) - \nabla\vec{E}_{\ell oc} \cdot \vec{S}_{oo} + \cdots \qquad (9)$$

where $\nabla\vec{E}_{\ell oc}$ is defined as

$$\nabla\vec{E}_{\ell oc} \equiv (\hat{x} + \hat{y})[\nabla_x\vec{E}_{dip}(\vec{r}) + \nabla_x\vec{E}_{dip,I}(\vec{r})] + \hat{z}[-\nabla_z\vec{E}_{dip}(\vec{r}) + \nabla_z\vec{E}_{dip,I}(\vec{r})].$$

Since $2e\vec{S}_{oo}(t)$ is the induced oscillating dipole at frequency ω, the second term in Eq. (9) describes an oscillation at 2ω, and the higher-order terms oscillations at higher harmonics. Thus, the local field contains not only the incoming frequency ω, but also all the harmonic frequencies. In case two frequencies ω_1 and ω_2 are present in the incoming wave, the local field should contain all the mixed frequencies $m\omega_1 + n\omega_2$, with m and n being integers. As a result, the induced polarization on the molecules will have all the harmonic or mixed frequency components. This appears as an additional contributuion to the apparent nonlinearity of the adsorbed molecules.[8,9]

III. LINEAR AND NONLINEAR POLARIZABILITIES OF ADSORBATES

We now discuss the derivation of linear and second-order nonlinear polarizabilities of molecules adsorbed on a substrate. For simplicity, we shall assume a single monochromatic incident beam at ω. The interaction Hamiltonian for an adsorbed molecule in the local electro-magnetic field is

$$\mathcal{H}_{int} = \frac{e}{2mc} [\vec{p} \cdot \vec{A}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\}) + \vec{A}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\}) \cdot \vec{p}]$$

$$+ \frac{e^2}{2m^2c^2} \vec{A}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\}) \cdot \vec{A}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\}) \tag{10}$$

where $\vec{A}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\})$ is the vector potential of the local field at $\vec{r}$ with the center of the induced and image dipoles at $\{\vec{S}_{ij}\}$. Having

$$\vec{E}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\}) = - \frac{1}{c} \frac{\partial}{\partial t} \vec{A}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\}) \tag{11}$$

we obtain, from Eq. (9), the funadmental and second harmonic frequency components of $\mathcal{H}_{int}$ as

$$\mathcal{H}_1(\omega) = \frac{e}{im\omega} \vec{p} \cdot \vec{E}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\})$$

$$\mathcal{H}_2(2\omega) = \frac{i}{2m\omega} \vec{p} \cdot \nabla\vec{E}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\}) \cdot \vec{\mu}(\omega) - \frac{e^2}{2m\omega^2} \left[\vec{E}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\})\right]^2 . \tag{12}$$

To find the polarizabilities, we use the following procedure. The current density operator is

$$\vec{J}(\vec{r}) = - \frac{e}{m} \left[\vec{p} + \frac{e}{c} \vec{A}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{S}_{ij}\})\right] \tag{13}$$

which can be decomposed into

$$\vec{J} = \vec{J}(0) + \vec{J}(\omega) + \vec{J}(2\omega) + - - -$$

$$\vec{J}(0) = -\frac{e}{m}\vec{p}$$

$$\vec{J}(\omega) = -\frac{e^2}{im\omega}\vec{E}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\})$$

$$\vec{J}(2\omega) = -\frac{e^2}{im\omega}\nabla\vec{E}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\}) \cdot \vec{\mu}(\omega). \tag{14}$$

We then notice that the time-average expectation value of $\vec{J} \cdot \vec{A}$ can be written as

$$\langle\vec{J} \cdot \vec{A}\rangle_{time} = \vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})^* \cdot \overleftrightarrow{\alpha}^{(1)}(\omega) \cdot \vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})$$

$$+ \vec{E}^{(2\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})^* \cdot \overleftrightarrow{\alpha}^{(2)}(2\omega) \cdot \vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})\vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})$$

$$+ - - - . \tag{15}$$

Using the density matrix formalism to carry out the perturbation calculation, we can identify

$$\vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})^* \cdot \overleftrightarrow{\alpha}^{(1)}(\omega) \cdot \vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\}) = \mathrm{Tr}\Big\{\vec{A}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\})^* \cdot [\vec{J}(0)\rho(\omega)$$

$$+ \vec{J}(\omega)\rho(0)]\Big\}$$

cont'd

$$\vec{E}^{(2\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})^* \cdot \alpha^{(2)}(2\omega) \cdot \vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})\vec{E}^{(\omega)}_{\ell oc}(0, \{\vec{R}_{ij}\})$$

$$= \mathrm{Tr}\left\{\vec{A}^{(2\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\})^* \cdot [\vec{J}(0)\rho(2\omega) + \vec{J}(\omega)\rho(\omega) + \vec{J}(2\omega)\rho(0)]\right\} \qquad (16)$$

where the density matrix ρ can be decomposed into $\rho = \rho(0) + \rho(\omega) + \rho(2\omega) + - - -$. The perturbation calculation leads to the following expressions for the linear and second-order polarizabilities.

$$\alpha^{(1)}_{ij}(\omega) = -\frac{e^2}{m\omega^2}\sum_g \langle g|f^*_\omega(\vec{r})f_\omega(\vec{r})|g\rangle\delta_{ij}\rho_g(0)$$
$$- \frac{e^2}{m^2\omega^2}\sum_{g,m}\left[\frac{\langle g|f^*_\omega(\vec{r})p_i|m\rangle\langle m|p_j f_\omega(\vec{r})|g\rangle}{\hbar(\omega - \omega_{mg})}\right.$$
$$\left. + \frac{\langle m|f^*_\omega(\vec{r})p_i|g\rangle\langle g|p_j f_\omega(\vec{r})|m\rangle}{\hbar(\omega + \omega_{mg})}\right]\rho_g(0)$$

$$\alpha^{(2)}_{ijk}(2\omega) = + \frac{e}{2m\omega^2}\sum_g \langle g|f^*_{2\omega}(\vec{r})f_\omega(\vec{r})|g\rangle\delta_{ij}\frac{\nabla_\ell E^{(\omega)}_{\ell oc,j}(0, \{\vec{R}_{ij}\})\alpha^{(1)}_{\ell k}}{E^{(\omega)}_{\ell oc,j}(0, \{\vec{R}_{ij}\})}\rho_g(0)$$
$$+ \frac{e}{2m^2\omega^2}\sum_{g,m}\left[\frac{\langle g|f^*_{2\omega}(\vec{r})p_i|m\rangle\langle m|p_j f_\omega(\vec{r})|g\rangle}{\hbar(2\omega - \omega_{mg})}\right.$$
$$\left. + \frac{\langle m|f^*_{2\omega}(\vec{r})p_i|g\rangle\langle g|p_j f_\omega(\vec{r})|m\rangle}{\hbar(2\omega + \omega_{mg})}\right]\frac{\nabla_\ell E^{(\omega)}_{\ell oc,j}(0, \{\vec{R}_{ij}\})}{E^{(\omega)}_{\ell oc,j}(0, \{\vec{R}_{ij}\})}\alpha^{(1)}_{\ell k}\rho_g(0)$$
$$- \frac{e^3}{i4m^2\omega^3}\sum_{g,m}\left[\frac{\langle g|f^*_{2\omega}(\vec{r})p_i|m\rangle\langle m|f_\omega(\vec{r})f_\omega(\vec{r})|g\rangle}{\hbar(2\omega - \omega_{mg})}\right.$$
$$\left. + \frac{\langle m|f^*_{2\omega}(\vec{r})p_i|g\rangle\langle g|f_\omega(\vec{r})f_\omega(\vec{r})|m\rangle}{\hbar(2\omega + \omega_{mg})}\right]\rho_g(0)$$
$$- \frac{e^3}{i2m^2\omega^3}\sum_{g,m}\left[\frac{\langle g|f^*_{2\omega}(\vec{r})f_\omega(\vec{r})|m\rangle\langle m|p_k f_\omega(\vec{r})|g\rangle}{\hbar(\omega - \omega_{mg})}\right.$$

cont'd

$$+ \frac{\langle m|f^*_{2\omega}(\vec{r})f_\omega(\vec{r})|g\rangle\langle g|p_k f_\omega(\vec{r})|m\rangle}{\hbar(\omega + \omega_{mg})}\Bigg]\rho_g(0)$$

$$- \frac{e^3}{i2m^3\omega^3}\sum_{g,m,n}\Bigg[\frac{\langle g|f^*_{2\omega}(\vec{r})p_i|m\rangle\langle m|p_j f_\omega(\vec{r})|n\rangle\langle n|p_k f_\omega(\vec{r})|g\rangle}{\hbar^2(2\omega - \omega_{mg})(\omega - \omega_{ng})}$$

$$- \frac{\langle m|f^*_{2\omega}(\vec{r})p_i|n\rangle\langle n|p_j f_\omega(\vec{r})|g\rangle\langle g|p_k f_\omega(\vec{r})|m\rangle}{\hbar^2(\omega + \omega_{mg})(\omega - \omega_{ng})}$$

$$+ \frac{\langle n|f^*_{2\omega}(\vec{r})p_i|g\rangle\langle g|p_j f_\omega(\vec{r})|m\rangle\langle m|p_k f_\omega(\vec{r})|n\rangle}{\hbar^2(\omega + \omega_{mg})(2\omega + \omega_{ng})}\Bigg]\rho_g(0) \qquad (17)$$

where we have defined $f_\omega(\vec{r}) = \vec{E}^{(\omega)}_{\ell oc}(\vec{r}, \{\vec{R}_{ij}\})/\vec{E}_{\ell oc}(0, \{\vec{R}_{ij}\})$.

The above expressions reduce to the usual ones for a free molecule if $f_\omega(\vec{r})$ is replaced by $\exp(i\vec{k}\cdot\vec{r})$ and if the first two terms in $\alpha^{(2)}_{ijk}$ are dropped. With the molecules adsorbed on the substrate, the spatial variation of the local field at the molecules can become quite significant over the molecular dimension. As a result, the matrix element $\langle m|f_\omega(\vec{r})\vec{p}|n\rangle$ can be very different from $\langle m|\vec{p}|n\rangle$. In particular, because $f(\vec{r})$ is neither odd nor even in $\vec{r}$, there no longer exists a parity selection rule for the transition matrix elements. The first two terms in $\alpha^{(2)}_{ijk}(2\omega)$ of Eq. (17) arise from the 2ω frequency component of the local field. They are proportional to the gradients of the dipole fields at the molecules. We notice that these terms, in fact, describe the same second-order polarizability discussed by Antoniewicz[8] using a simple image-dipole model with the spatial variation $f(\vec{r})$ neglected, but the problem we have treated here is more general.

If we now incorporate the local field correction factor L into the polarizabilities in the usual way, we find the effective linear and second-

order polarizabilities as

$$\left[\alpha_{ij}^{(1)}(\omega)\right]_{eff} = L_{ii}(\omega)\alpha_{ij}^{(1)}(\omega)L_{jj}(\omega) \tag{18}$$

if the incoming and outgoing waves are of different modes;

$$\left[\alpha_{ii}^{(1)}(\omega)\right]_{eff} = \alpha_{ii}^{(1)}(\omega)L_{ii}(\omega) \tag{19}$$

if the incoming and outgoing waves are of the same mode; and

$$\left[\alpha_{ijk}^{(2)}(\omega = \omega_1 + \omega_2)\right]_{eff} = L_{ii}(\omega)\alpha_{ijk}^{(2)}L_{jj}(\omega_1)L_{kk}(\omega_2). \tag{20}$$

IV. DISCUSSION

The results in Sec. III show that the local field arising from the electromagnetic interaction can significantly modify the polarizabilities of the adsorbed molecules. In comparison with the case of free molecules in the gas phase, the modification comes in two ways. First, the average local field at the adsorbed molecules leads to a local field correction factor $\overleftrightarrow{L}$ for each independent field component attached to the polarizabilities. Then, the rapid spatial variations of the local fields at the molecules can yield transition matrix elements very different from the usual dipole matrix elements. In the nonlinear case, the local field can further modify the polarizabilities via its harmonic or mixed frequency components. Because the local field here results from the induced dipole-induced dipole and induced dipole-image dipole interaction,[5] its deviation from the applied field is expected to increase monotonically with increase

of the surface molecular density, increase of molecular polarizability, increase of the reflectivity of the substrate, and decrease of the distance of the adsorbed molecules from the substrate.

If the closest distance between adsorbed molecules is smaller than or comparable to the distance of the adsorbed molecules from the substrate, the induced dipole-induced dipole interaction between the adsorbed molecules is mainly responsible for the local field correction factor. This is because the dipole-dipole interaction is of short range, and a molecule sees several induced dipoles but only one image dipole at its nearest neighbor sites. In such a case, L_{xx} and L_{yy} should be less than 1, and L_{zz} should be larger than 1, as we have already mentioned in Sec. III. An explicit example is shown in Fig. 1. There, with $\varepsilon = 10$ and $a = 5$ Å, the contributions of the image dipoles to $L_{xx} = L_{yy}$ and L_{zz} are seen to have dropped to nearly zero for $Z_o \gtrsim 2.3$ Å. For smaller values of ε, the image dipole effect is even weaker. If ε is 3 instead of 10 in Fig. 1, then the image dipole contribution to $\overleftrightarrow{L}$ is negligible for $Z_o > 2$ Å, and if $\varepsilon = 1.5$, it is negligible for $Z_o > 1.7$ Å. Clearly, with a smaller surface coverage of molecules, i.e., a larger "a", the local field correction should become less important (with $\overleftrightarrow{L}$ close to 1), but the relative importance of the image dipole contribution to $\overleftrightarrow{L}$ is expected to increase.

As we have remarked earlier, only the "average" local field at the molecules is described by the local field correction factor. Therefore, it should not change the selection rules of the transition matrix elements. However, the local field at the adsorbed molecules can actually have a significant variation over the molecular dimensions. Such a rapid spatial variation indicates that the multipole contribution in the transi-

tion matrix elements is non-negligible for the adsorbed molecules. As a result, the usual selection rules for electric dipole transitions are no longer applicable here. A direct consequence of this is that even for a centrosymmetric molecule very weakly adsorbed on substrates, it can have a significant $\overleftrightarrow{\alpha}^{(2)}$.

We have used $f(\vec{r})$ in the matrix elements of Eq. (17) to describe the spatial variation of the local field across a molecule. Strictly speaking, $f(\vec{r})$ should be a tensor, but we expect, from dipole-dipole interaction, that the tensorial character of $f(\vec{r})$ is weak. The variation of the local field is mainly along the surface normal $\hat{z}$, and is due to induced dipole-image dipole interaction. Therefore, it is more significant if the adsorbed molecules are closer to the substrate and the dielectric constant of the substrate is larger. An example of how $f(\vec{r}) \simeq f(z)$ varies with z is shown in Fig. 2, assuming $Z_o = \frac{1}{3}\,a = 1.7$ Å and $\varepsilon = 10$. The strong variation of $f(\vec{r})$ over a molecular dimension indicates that the electric-dipole approximation used to calculate polarizabilities is no longer valid. However, as Z_o increases, the dependence of f(z) on z quickly diminishes. To estimate the importance of f(z), we divide f(z) into symmetric and antisymmetric parts, $f(z) = f_s(z) + f_a(z)$, and define a ratio $\phi = [f_a(z)/f_s(z)]_{z=r_o}$, where r_o denotes roughly the half size of the molecules. Note that to the first order, $f_s \simeq 1$, and $f_a(z) = z\left(\frac{\partial}{\partial z} E_{\ell oc}\right)_o / E_{\ell oc}(0)$. With r_o chosen to be 0.7 Å, we find, for $\alpha_{zz}^{(1)} = 10$ Å and $\varepsilon = \infty$, the ratio ϕ is larger than 0.1 only when $Z_o < 2.3$ Å. For $\varepsilon = 3$ and $\varepsilon = 1.5$, we find $\phi > 0.1$ only when $Z_o < 1.8$ Å and 1.6 Å, respectively. If $\alpha_{zz}^{(1)}$ becomes 5 Å instead, then for $\varepsilon = \infty$, 3, and 1.5, we have $\phi > 0.1$ when $z_o < 1.8$ Å, 1.6 Å, and 1.3 Å, respectively. Thus, crudely speaking, if the center of an

adsorbed molecule (i.e., center of the electronic cloud responsible for the linear polarizability) is more than 2.5 Å away from a substrate, the spatial variation of the local field has negligible effect on the polarizabilities. On the other hand, if the center of the molecule is less than 1.5 Å away from a substrate, the spatial variation of the local field can modify the polarizabilities appreciably. In the latter case, a centrosymmetric molecule can have a significant second-order nonlinear polarizability even if the distortion of wavefunctions due to adsorption is negligible.

As pointed out by Antoniewicz,[7] the linear response of the molecule to the second-harmonic or mixed frequency component of the local field can also contribute to the second-order nonlinearity of the absorbed molecules. This effective nonlinearity is proportional to the dipole field gradients at the molecules, as shown explicitly in the first two terms of $\alpha^{(2)}_{ijk}$ in Eq. (17), and therefore, it increases rapidly as Z_o decreases. However, it is probably at most of the same order as the other terms in Eq. (17). This can be seen as follows. Assume centrosymmetric molecules so that $\alpha^{(2)} \simeq 0$ in the absence of local field. If we use the approximation of $f(z) = 1$ in the electric-dipole allowed matrix elements and $f(z) = 1 + z\left(\frac{\partial}{\partial z} E_{\ell oc}(z)\right)_o / E_{\ell oc}(0)$ in the electric-dipole forbidden matrix elements in Eq. (17), then with ω and 2ω far away from resonances, we can simplify the expression of $\alpha^{(2)}_{ijk}$ by the closure property of the eigenstates. The first two terms of $\alpha^{(2)}_{ijk}$ in Eq. (17) become

$$|\alpha^{(2)}_{ijk}|_1 = \frac{2}{e}\, \alpha^{(1)}_{ij}\, \alpha^{(1)}_{\ell k}\, \nabla_\ell E^{(\omega)}_{\ell oc,j}(0, \{R_{ij}\}) / E^{(\omega)}_{\ell oc,j}(0, \{R_{ij}\})$$

cont'd

$$\sim 2e^3(\langle r^2\rangle)^2\left(\frac{\partial}{\partial z} E_{\ell oc}(z)\right)_o / E_{\ell oc}(0). \tag{21}$$

The rest of the terms of $\alpha^{(2)}_{ijk}$ in Eq. (17) becomes

$$|\alpha^{(2)}_{ijk}|_2 \sim 3e^3\langle r^4\rangle\left(\frac{\partial}{\partial z} E_{\ell oc}(z)\right)_o / E_{\ell oc}(0). \tag{22}$$

Since $\langle r^4\rangle$ is always larger than $\langle r^2\rangle^2$, we have $|\alpha^{(2)}_{ijk}|_1 < |\alpha^{(2)}_{ijk}|_2$. In the case where the ground state wavefunction is more spread out, a larger difference is expected. As an example, we use the $3p_z$ wavefunction of Ar, $\psi = Nzr\exp(-r/0.444)$, to calculate $\langle r^2\rangle$ and $\langle r^4\rangle$, and find $|\alpha^{(2)}_{zzz}|_1 / |\alpha^{(2)}_{zzz}|_2 \sim 0.4$. A more careful calculation taking into account the higher order terms in f(z) gives even a much smaller ratio. This makes us believe that the effective second-order nonlinearity arising from the linear response of the molecule to the second-harmonic frequency component of the local field is not as important as that arising from the nonlinear response to the fundamental component of the spatially varying local field.

For non-centrosymmetric molecules, $\alpha^{(2)}$ is nonvanishing even in the absence of local field. The local-field contribution to $\alpha^{(2)}$ via $f(\vec{r})$ becomes comparable to the intrinsic $\alpha^{(2)}$ only when $|\langle f_a(\vec{r})\rangle| \sim |\langle f_s(\vec{r})\rangle|$. Then, according to our earlier estimates, the local field variation has a large effect on $\alpha^{(2)}$ only when the distance of the molecules from the substrate, Z_o, is small, say, less than ~ 1.5 Å, and in all cases, the contribution from the linear response to the second harmonic component of the local field is small compared to the instrinsic $\alpha^{(2)}$.

V. CONCLUSION

From what we have discussed, we can arrive at the following conclusion. The electromagnetic interaction between molecules and between the molecules and the substrate can be accounted by the local field effect. It appears in two respects: a local field correction factor arising from the spatially non-varying part of the local field at the molecules, and a modification of the transition matrix elements in the polarizabilities by the spatially varying part of the local field. The harmonic and mixed frequency components of the local field play a relatively unimportant role.

For typical molecules with $\alpha^{(1)} \lesssim 10$ Å, that part of the local-field correction factor coming from the molecule-substrate interaction is negligible if the adsorbed molecules are more than 2.5 Å away from the substrate in the case of a metal substrate, or more than 1.5 Å away in the case of an insulator with $\varepsilon \sim 1.5$. The part of the local field correction factor coming from the molecule-molecule interaction is negligible (i.e., $|L_{ii} - 1| < 0.1$) if the nearest neighbor distance, "a", between the adsorbed molecules is larger than 10 Å. When the molecule-molecule interaction dominates, L_{xx}, L_{yy} are less than 1, and L_{zz} larger than 1. When the molecule-susbstrate interaction dominates, all L_{ii} are larger than 1.

The spatially varying part of the local field at the molecules can give rise to multipole contribution to the matrix elements involved in the polarizabilities. Accordingly, the electric-dipole selection rules for the polarizabilities are broken. This part arises mainly from the molecule-substrate interaction. For $\alpha^{(1)} \lesssim 10$ Å, it is negligible if the molecules are more than 2.5 Å away from a substrate, but it can strongly modify the molecular polarizabilities if the molecule is less than ~ 1.5 Å

away from the substrate. In the latter case, a centrosymmetric molecule may appear to have a second-order nonlinear polarizability as large as a non-centrosymmetric molecule.

We now consider the more general case where the eigenstates of the molecules are distorted by the "chemical interaction" upon adsorption. Clearly, the effect of the electromagnetic interaciton should appear on top of the chemical interaction. Our discussion here should therefore apply to this general case as long as the proper eigenstates of the molecules are used. Both the local field correction factor and the spatially varying local field component should still contribute to the effective polarizabilities. In fact, for chemically adsorbed molecules, because of the bond formation between the molecules and the substrate, the effective distance between the molecules and the substrate is expected to be small, and hence, the local field effect should be more important than in the physically adsorbed case. This is particularly true for metal substrates. Following this argument, we expect that if a relatively small molecule is chemically adsorbed on a metal surface, its polarizabilities can be drastically modified by the local field. In particular, a relatively large second-order nonlinearity may result for a centrosymmetric molecule even if its symmetry is not appreciably distorted by the chemical interaction.

In experiments using a second-order nonlinear optical process to probe adsorbed molecules, the nonlinear susceptibility $\overleftrightarrow{\chi}^{(2)}$, instead of the polarizability $\overleftrightarrow{\alpha}^{(2)}$, is measured. The symmetry of $\overleftrightarrow{\chi}^{(2)}$ reflects the symmetry of the molecular arrangement on the surface, while the ratios of non-vanishing $\chi^{(2)}$ elements reflect the molecular orientation on the surface. We note that the local field has no effect on the symmetry of $\overleftrightarrow{\chi}^{(2)}$, but

it does modify the effective $\alpha^{(2)}_{ijk}$ through both the local-field correction factor and the spatially varying component of the local field. This makes the determination of molecular orientation from the $\overleftrightarrow{\chi}^{(2)}$ measurement complicated if the local field effect is not negligible or known.

REFERENCES

1. C. K. Chen, A. R. B. de Castro, Y. R. Shen, and F. DeMartini, Phys. Rev. Lett. 43, 946 (1979); 46, 145 (1981); J. P. Heritage and P. L. Allara, Chem. Phys. Lett. 74, 507 (1980).

2. C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. 46, 1010 (1981); T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. 48, 478 (1982).

3. D. M. News, Phys. Rev. B 1, 3304 (1970); D. E. Beck and V. Celli, Phys. Rev. B 2, 2955 (1970).

4. G. D. Mahen and A. A. Lucas, J. Chem. Phys. 68, 1344 (1978); F. W. King, R. P. Van Duyne, and G. C. Schatz, J. Chem. Phys. 69, 4472 (1978); G. L. Eesley and J. R. Smith, Solid State Commun. 31, 815 (1979).

5. A. Bagchi, R. G. Barrera, and B. B. Dasgupta, Phys. Rev. Lett. 44, 1475 (1980); A. Bagchi, R. G. Barrera, and R. Fuchs, Phys. Rev. B 25, 7086 (1982).

6. N. Bloembergen, Nonlinear Optics (Benjamin, Inc., New York, 1965), p. 192.

7. P. R. Antoniewicz, Phys. Rev. B 26, 2285 (1982).

8. T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, Chem. Phys. Lett. 83, 180 (1981).

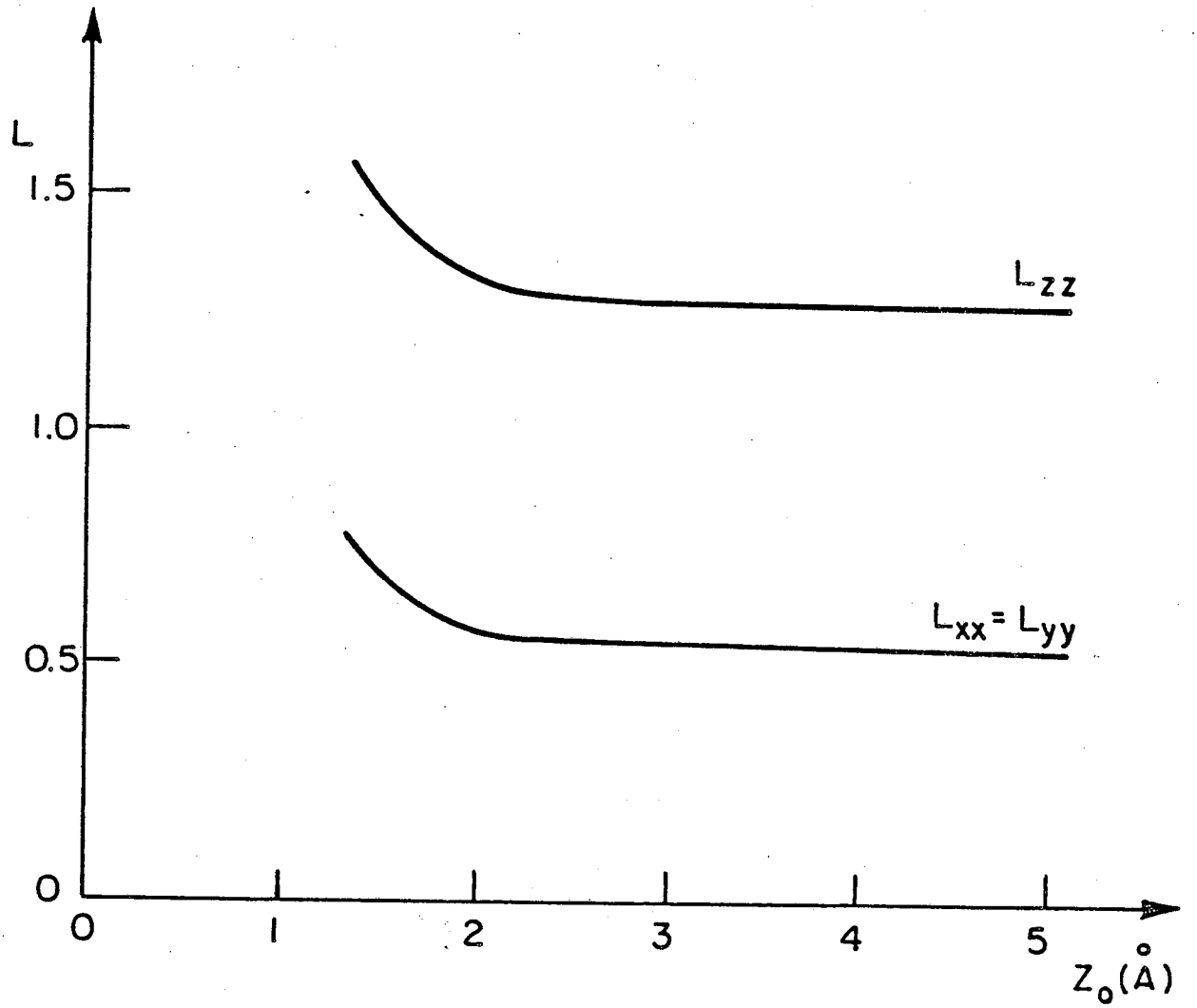
9. G. C. Schatz and R. P. Van Duyne, Surf. Sci. 101, 425 (1980); S. Efrima and H. Metiu, J. Chem. Phys. 70, 1602 (1979); 70, 2297 (1979); T. Maniv and H. Metiu, J. Chem. Phys. 72, 1996 (1980); W. H. Weber and G. W. Ford, Phys. Rev. Lett. 44, 1774 (1980); G. W. Ford and W. H. Weber, Surf. Sci. 109, 451 (1981).

10. J. Fiutak, Can. J. Phys. 41, 12 (1963); E. Adler, Phys. Rev. 134 A728 (1964).

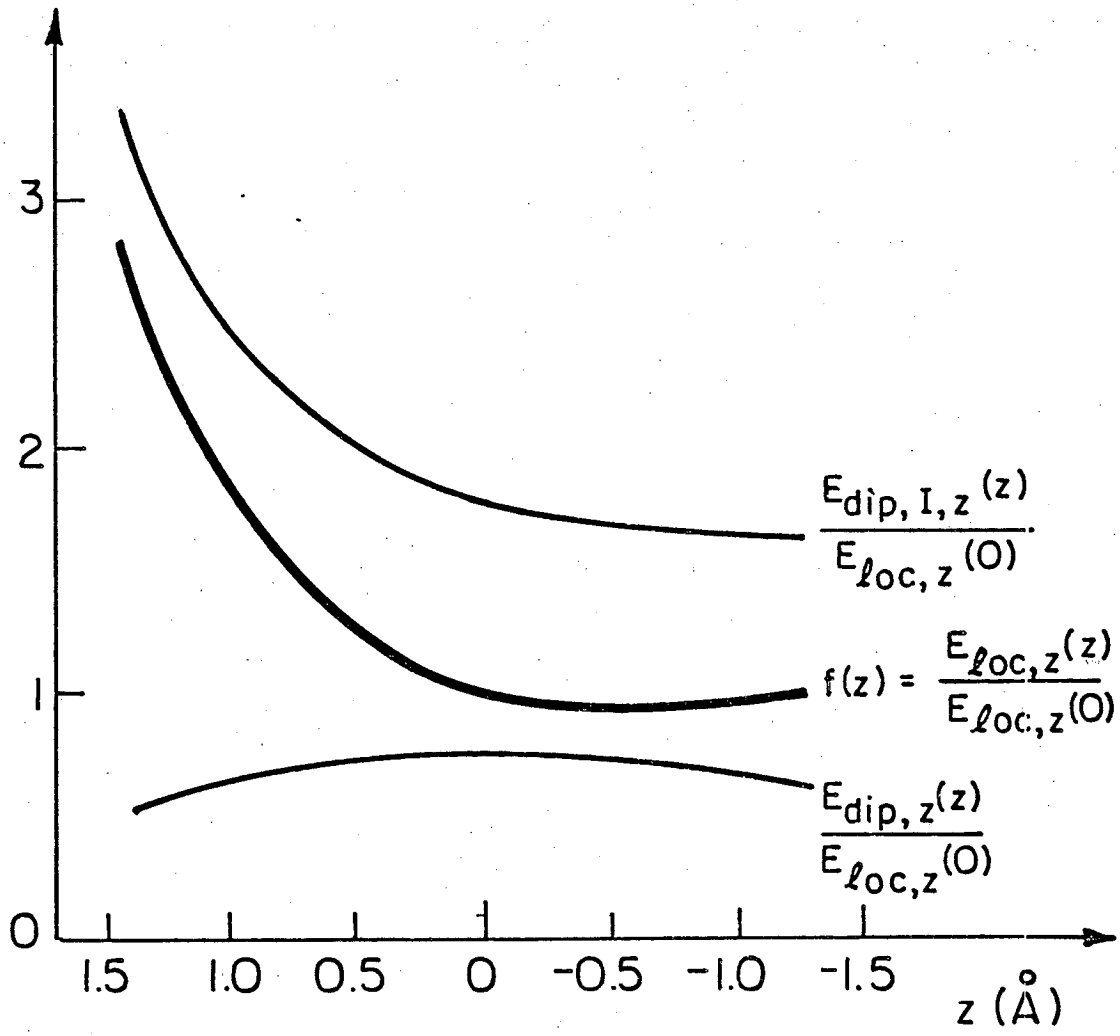
FIGURE CAPTIONS

Fig. 1 Local field correction factors calculated from the point-dipole model as a function of the distance of molecules from the substrate, assuming a = 5 Å, α_{xx} = 6 Å and α_{zz} = 11 Å for adsorbed molecules, and ε = 10 for the substrate.

Fig. 2 Local field variation along the surface normal around a molecule. Contributions from the induced dipole-induced dipole interaction and from the induced dipole-image dipole interaction are denoted by $E_{dip,z}(z)$ and $E_{dip,I,z}(z)$, respectively.



XBL 835-5583


3
2
1
0
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
z (Å)
$\frac{E_{dip,I,z}(z)}{E_{loc,z}(0)}$
$f(z) = \frac{E_{loc,z}(z)}{E_{loc,z}(0)}$
$\frac{E_{dip,z}(z)}{E_{loc,z}(0)}$

XBL 835-5582

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720