

Vibrational interaction between molecules adsorbed on a metal surface: The dipole-dipole interaction

B. N. J. Persson

*Institut für Festkörperforschung der Kernforschungsanlage Jülich GmbH,
Postfach 1913, D-5170 Jülich 1, Federal Republic of Germany*

R. Ryberg

Chalmers University of Technology, Department of Physics, S-412 96 Gothenburg, Sweden

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We have developed a theory for the properties of vibrational excitations in molecules adsorbed on a metal surface. The coherent potential approximation (CPA) is used in the treatment of the vibrational interaction between the molecules. We show, by interpreting infrared spectra of substitutionally disordered systems consisting of isotopic mixtures of CO on Cu(100), that the molecules interact mainly through their dipole fields. We also show that in interpreting the integrated absorptance in infrared spectroscopy or the relative loss intensity in electron-energy-loss spectroscopy it is necessary to take into account the screening due to the electronic polarizability of the adsorbed molecules. A simplified version of the CPA result is used for a discussion of the absorption spectra of partial monolayers of one isotope. With the assumption that the CO molecules are randomly distributed, comparison between theory and experiment indicates that the dipole-dipole interaction alone is responsible for the coverage-dependent frequency shift for CO adsorbed on a transition metal [Ru(001)]; whereas there is an almost equally large counteracting chemical shift on a noble metal [Cu(100)]. The meaning and origin of the dynamical dipole moment of adsorbed CO molecules are discussed. We find that the increase of the dynamical dipole moment (by a factor 2–3) upon adsorption probably is due to charge oscillations between CO $2\pi^*$ molecular orbitals and the metal. Finally, we outline how the theory developed here can be applied to a fundamental step in photosynthesis.

I. INTRODUCTION

Infrared spectroscopy (IRS) has proved to be a very useful tool for studies of vibrationally excited molecules adsorbed on a metal surface. In these experiments a beam of monoenergetic photons is incident upon the adsorbate covered metal surface. In the infrared region the main part (90–99%) of the photons will be reflected by the metal. A “dip” in the number of reflected photons (a few percent or less) will, however, be found at those photon energies which correspond to vibrational excitation energies of the adsorbed molecules.

Consider a beam of photons incident upon a metal surface. If I and I' are, respectively, the intensity of the reflected beam with and without adsorbed molecules, then the change in reflectance, due to the adsorbed molecules, is defined by

$$\Delta = \frac{I' - I}{I}$$

By varying the energy $\hbar\omega$ of the incident photons one gets a function $\Delta(\omega)$ which is different from zero only in small regions around the vibrational frequencies Ω of the excitations in the monolayer. The function $\Delta(\omega)$ is the primary information one obtains from an IRS experiment.

Adsorbed molecules on a metal surface will interact with each other and this interaction affects many of the measurable properties of the system; in particular, when calculating $\Delta(\omega)$ it is necessary to know this interaction.¹ Assume, for example, that we have an ordered monolayer of one adsorbed species A . Due to the interaction between the molecules, the vibrational eigenmodes will not be localized vibrations but rather “phonon modes” characterized by a two-dimensional wave vector \vec{q} (taking values within the Brillouin zone determined by the geometry of the monolayer), and with different energies $\hbar\Omega(\vec{q})$. Since the photons (wave vector \vec{k}) have $\vec{k} \simeq 0$ (compared with $1/a$, where a is the distance between two nearest-neighbor

molecules), only the $\vec{q}=0$ mode can be excited, due to momentum conservation. It follows that an experiment of this kind can only depend on the $\vec{q}=0$ component of the interaction potential $\tilde{U}(\vec{q})$.

However, it is possible to measure the whole function $\tilde{U}(\vec{q})$ in an IRS experiment, if one can *break* the translational invariance in the monolayer. A complete monolayer of an *isotopic mixture* is such a system. The change in reflectance, $\Delta(\omega)$, of this system will depend on the whole interaction potential $\tilde{U}(\vec{q})$. By measuring $\Delta(\omega)$ as a function of the concentration of the different isotopes in the monolayer it should, in principle at least, be possible to determine $\tilde{U}(\vec{q})$. Isotopic mixtures of $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ have previously been studied by IRS on Pt(111), Pt(100) (Ref. 2) and on Cu(111) (Ref. 3).

A more direct way to obtain $\tilde{U}(\vec{q})$ would be by electron-energy-loss spectroscopy (EELS). By analyzing the off-specular inelastically scattered electrons it is possible to obtain the dispersion relation $\Omega(\vec{q})$ and therefore also the interaction potential $\tilde{U}(\vec{q})$. Recently, Andersson and Persson⁴ have in this way obtained $\tilde{U}(\vec{q})$ for a monolayer of CO molecules adsorbed on a Cu(100) surface. The result of this experiment indicates that $\tilde{U}(\vec{q})$ for this system is mainly due to a dipole-dipole interaction between the adsorbed molecules. This is consistent with the conclusion obtained by us in an earlier paper⁵ and also in the present paper by analyzing the IRS spectra of isotopic mixtures.

In the present work we calculate $\Delta(\omega)$ for a complete monolayer of a mixture of several different kinds of molecules A, B, C, \dots . We assume that the molecules are randomly distributed over the sites of a Bravais net. This should be the case for an isotopic mixture and the theory will therefore be compared with experimental results we have obtained for mixtures of different CO isotopes adsorbed on Cu(100). As we shall see, the theory is in very good agreement with these results.

This paper is divided into a number of sections. In Sec. II we calculate the change in reflectance, $\Delta(\omega)$, for a complete monolayer of one single adsorbed specie A . In Sec. III we calculate (using the CPA) the same quantity under the assumption that the monolayer consists of a substitutional random mixture of different molecules A, B, C, \dots and in Secs. IV and V we discuss the implications of the resulting expression for $\Delta(\omega)$. In Sec. VI we compare theoretical and experimental results for isotopic mixtures of CO adsorbed on Cu(100). Section VII contains some further applications of the theory to the IRS spectra of incomplete mono-

layers. A general discussion of the interpretation of the dynamical dipole moment of chemisorbed molecules is given in Sec. VIII. In Sec. IX we show that the theory developed in Sec. III also can be used in a discussion of a fundamental step in photosynthesis. Section X, finally, contains a summary of the most important results obtained in this work.

II. $\Delta(\omega)$ FOR A MONOLAYER OF IDENTICAL MOLECULES

The change in reflectance for a system consisting of a complete monolayer of identical molecules adsorbed on a metal surface can be written as

$$\Delta(\omega) \sim n\omega \text{Im}\alpha_0(0, \omega), \quad (1)$$

where $\alpha_0(\vec{q}, \omega)$ is the polarizability of the monolayer and n is the number of adsorbed molecules per unit area. For completeness let us also point out that the relative loss intensity I_1/I_0 , measured in an EELS experiment, is proportional to⁴

$$\frac{I_1}{I_0} \sim \text{Im}\alpha_0(\vec{q}, \omega), \quad (2)$$

where \vec{q} is the change in the wave vector, parallel to the metal surface, of the inelastic scattered electrons. The proof of Eq. (1) is given in Appendix A.

Equations (1) and (2) are quite general and independent of the form of the interaction potential between the molecules. However, to calculate $\alpha_0(\vec{q}, \omega)$ we must specify this interaction. In the present work we assume that the vibrating molecules interact with each other only through their oscillating dipole fields ("dipole-dipole interaction"). The good agreement which is obtained between theory and experiment indicates that this assumption is correct for the systems considered in this work. However, in general one cannot exclude other types of interactions such as a direct overlap of the electronic wave functions of nearby molecules or an indirect interaction mediated by the electrons and ions of the metal.

Assume then that we have a monolayer of identical molecules A adsorbed on a metal surface. Let \vec{x}_i denote the position vector of molecule i and let p_i be the *induced* dipole moment caused by an external electric field \vec{E}_i . Owing to the large value of the dielectric function of the metal in the infrared region both p_i and E_i will be normal to the metal surface. We can therefore write

$$p_i = \alpha_A \left[E_i - \sum_{j \neq i} U_{ij} p_j \right], \quad (3)$$

where α_A is the polarizability of one single adsorbed molecule A and $-U_{ij} p_j$ is the electric field at \vec{x}_i from the dipole p_j and its image.⁶ That is

$$U_{ij} = \frac{1}{|\vec{x}_i - \vec{x}_j|^3} + \dots,$$

where the ellipsis represents the image contribution from p_j .

Equation (3) can be solved for p_i if we write

$$p_i = \sum_q p_q e^{i(\vec{q} \cdot \vec{x}_i - \omega t)},$$

$$E_i = \sum_q E_q e^{i(\vec{q} \cdot \vec{x}_i - \omega t)},$$

and so

$$p_q = \alpha_A [E_q - \tilde{U}(\vec{q}) p_q]$$

or

$$p_q = \frac{\alpha_A}{1 + \alpha_A \tilde{U}(\vec{q})} E_q \equiv \alpha_0(\vec{q}, \omega) E_q, \quad (4)$$

where

$$\tilde{U}(\vec{q}) = \sum_j U_{ij} e^{-i\vec{q} \cdot (\vec{x}_i - \vec{x}_j)}.$$

For energies $\hbar\omega$ in the infrared region we may write

$$\alpha_A = \alpha_e + \frac{\alpha_v}{1 - (\omega/\omega_A)(\omega/\omega_A + i\gamma)}, \quad (5)$$

where the electronic polarizability α_e is approximately independent of ω and where α_v is the vibrational polarizability. Equations (1) and (4) give

$$\Delta(\omega) \sim n\omega \operatorname{Im} \frac{\alpha_A}{1 + \alpha_A \tilde{U}(0)}. \quad (6)$$

If the damping γ in Eq. (5) is infinitesimally small then Eqs. (5) and (6) give

$$\Delta(\omega) \sim n\omega_A^2 \frac{\alpha_v}{[1 + \alpha_e \tilde{U}(0)]^2} \delta(\omega - \Omega), \quad (7)$$

where

$$\left[\frac{\Omega}{\omega_A} \right]^2 = 1 + \frac{\alpha_v \tilde{U}(0)}{1 + \alpha_e \tilde{U}(0)}. \quad (8)$$

We notice the following:

(a) Owing to the dipole interaction between the molecules the central frequency of the absorption

peak is shifted upwards from ω_A to Ω as given by Eq. (8). This expression has been derived and discussed by Mahan and Lucas⁷ and we refer the readers to their paper (see also Ref. 8).

(b) The area under the absorption peak is proportional to

$$\int d\omega \Delta(\omega) \sim \frac{\alpha_v}{[1 + \alpha_e \tilde{U}(0)]^2}. \quad (9)$$

This is a very important relation, which shows how the integrated absorptance depends on the dielectric screening due to the electronic polarizability of the molecules. In all previous theories for calculating the integrated absorptance in IRS, or the relative loss intensity in EELS,⁹ this screening has been neglected. This is certainly a bad approximation for CO on Cu(100) since it turns out that $\alpha_e \approx$ a few \AA^3 and $\tilde{U}(0) = 0.3 \text{\AA}^{-3}$, so that $\alpha_e \tilde{U}(0) \approx 1$. Consequently it is inadmissible to neglect the term $\alpha_e \tilde{U}(0)$ in the denominator of Eq. (7).

We can see from Eq. (7) that $\Delta(\omega)$ only depends on the $\vec{q}=0$ component of the interaction potential $\tilde{U}(\vec{q})$. As was emphasized already in the Introduction, this is simply a consequence of the translational invariance (by an arbitrary lattice vector) of the monolayer and by the smallness of the momentum carried by photons. In the next section, where we consider systems where this translational invariance is broken, we shall instead get a function $\Delta(\omega)$ which depends on the whole $\tilde{U}(\vec{q})$. More exactly, $\Delta(\omega)$ will depend on an integral over the Brillouin zone of the adsorbate lattice cell:

$$Q = \frac{1}{\mathcal{A}^*} \int_{\text{BZ}} d^2q \frac{\tilde{U}(\vec{q})}{1 + \alpha \tilde{U}(\vec{q})}, \quad (10)$$

where \mathcal{A}^* is the area of the Brillouin zone and where α , in general, is a complex number independent of \vec{q} . As a prelude to the next section, we now calculate Q . To be concrete we consider the system $c(2 \times 2)\text{CO}/\text{Cu}(100)$. The nearest-neighbor adsorbate distance is 3.61 \AA and, as has been determined from LEED intensity measurements,¹⁰ the center of mass of an adsorbed CO molecule is about 0.8 \AA above the "image plane" as defined in the jellium model¹¹ (see Fig. 1). It is then straightforward to calculate $\tilde{U}(\vec{q})$ numerically. In Fig. 2(b) we show the resulting $\tilde{U}(\vec{q})$ for two directions [$\vec{q} = (1,0)$ and $\vec{q} = (1,1)$] in the reciprocal-lattice cell. Now, in performing the integral (10) we replace this cell, which is a square, by a circle of radius q_0 with the same area \mathcal{A}^* as the original cell

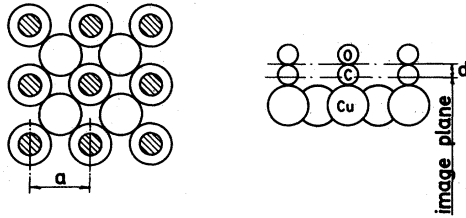


FIG. 1. The $c(2 \times 2)$ structure of CO on Cu(100). a is the adsorbate lattice constant (3.61 Å) and d is the height above the image plane of the center of mass of the CO molecule (0.8 Å).

$$\pi q_0^2 = \mathcal{A}^* = \left(\frac{2\pi}{a} \right)^2,$$

where a is the adsorbate lattice constant. Moreover, we have approximated $\tilde{U}(\vec{q})$ by a function $\tilde{U}(q)$ depending only on the magnitude of \vec{q} :

$$\tilde{U}(q) = U_0 \left[1 + A \frac{q}{q_0} + B \left(\frac{q}{q_0} \right)^2 \right]. \quad (11)$$

U_0 , A , and B were chosen to give the best possible fit¹² to the numerical curves in Fig. 2(b). The dotted curve is the result with

$$U_0 = 0.3 \text{ Å}^{-3}, \quad A = -2.4, \quad B = 1.2. \quad (12)$$

Note that $\tilde{U}(q)$ is an extremely good approximation for $q \lesssim 2/a$ and that for $q \gtrsim 2/a$ it is essentially the angular average of $\tilde{U}(\vec{q})$.

After having specified $\tilde{U}(q)$ it is easy to calculate the integral Q . The result is

$$Q = \frac{1}{\alpha} \left[1 - \frac{\xi}{1.2} \left[\ln \frac{\xi - 0.2}{\xi + 1} + \frac{1}{\xi} \ln \frac{\xi - 1}{\xi + 1} \right] \right], \quad (13)$$

where $\xi = 1/\alpha U_0$ and $\zeta = [(0.2 - \xi)/1.2]^{1/2}$. Q is treated as an analytical function of α with the logarithmic and square-root branch cuts along the negative real axis.

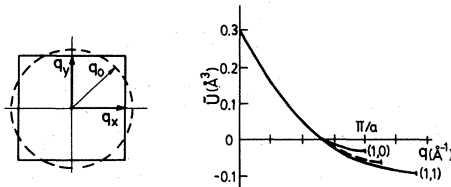


FIG. 2. (a) The first Brillouin zone of the adsorbate lattice shown in Fig. 1. (b) The spatial Fourier transform $\tilde{U}(\vec{q})$ of the dipole field for two directions in the Brillouin-zone. The dotted curve is the directionally independent approximation.

III. $\Delta(\omega)$ FOR A SUBSTITUTIONALLY DISORDERED MONOLAYER

The stationary vibrational states of a complete monolayer of identical adsorbates are plane waves. This is a direct consequence of the translational invariance of the interaction potential between the molecules. But if we have different kinds of adsorbed molecules the stationary states are no longer plane waves. The function $\Delta(\omega)$ can now only be calculated approximately. Using the so-called CPA¹³ we have calculated a quite general expression for $\Delta(\omega)$ within the following model: Assume that at site \vec{x}_i on the metal surface there is an adsorbed molecule having the polarizability α_i and the induced dipole moment p_i . We allow the polarizabilities α_i to vary from site to site corresponding to having different kinds of adsorbed molecules. (Note that by choosing $\alpha_i = 0$ for some \vec{x}_i we get as a special case a partially filled monolayer.) We have assumed that the molecules are stochastically distributed among the sites. The basic equation from which $\Delta(\omega)$ can be calculated is

$$p_i = \alpha_i \left[E_i - \sum_j U_{ij} p_j \right] \quad (14)$$

which is a generalization of Eq. (3) to the case where the adsorbate molecules have different polarizabilities α_i . Equation (14) can be iterated

$$p_i = \alpha_i E_i + \sum_j \alpha_i (-U_{ij}) \alpha_j E_j + \dots \quad (15)$$

We visualize each term in this expansion as follows: The molecule at x_i can be excited either directly by absorption of a photon (the first term) or a photon may first excite another molecule at x_j , followed by a jump (due to the dipole-dipole coupling U_{ij}) of the excitation to the molecule at x_i (the second term) and so on.

Before we apply the CPA to Eq. (15) let us first briefly sketch the spirit of this approximation. Figure 3(a) shows a possible configuration of a substitutionally disordered monolayer with two types of molecules A and B . Physical quantities of interest, such as the polarizability of the monolayer, are not those of a particular configuration, but those averaged over the ensemble of possible configurations. Therefore this ensemble is replaced by a system schematically drawn in Fig. 3(b), i.e., a periodic system with the same "ensemble average" polarizability α at each site. The most important problem is to find a reasonable procedure to determine the polarizability α which describes the

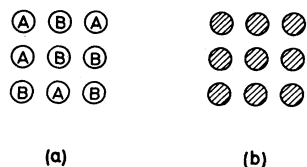


FIG. 3. (a) A possible configuration of a substitutionally disordered monolayer of A and B molecules. (b) In the CPA the ensemble of all possible configurations is represented by a system with an average molecule at each site.

“average” molecule. According to the CPA this quantity can be determined in a self-consistent way by the following procedure: Assume that each site except for the origin is occupied by the “average” molecule and the origin by molecule A or B , as shown in Fig. 4. Then we calculate the induced dipole moment (due to a given external electric field) of the molecule at the origin, denoted by p_A or p_B . Finally we calculate the induced dipole moment p of the molecule at the origin when this is occupied by an “average” molecule. α is then obtained from

$$c_A p_A + c_B p_B = p, \quad (16)$$

where c_A is the concentration of molecules A and c_B of molecules B ($c_A + c_B = 1$).

After having sketched the essence of the CPA we now perform the actual calculation. Assume that the external electric field is given by

$$E_i = E(\vec{q}) \cdot e^{i(\vec{q} \cdot \vec{x}_i - \omega t)}$$

p_A in Eq. (16) can then be calculated as follows. We obtain from Eq. (15) (note: $\vec{x}_i = 0$ at the position of molecule A)

$$p_A = \alpha_A \left[1 + \sum_j V_{Aj} \alpha_j + \sum_{jk} V_{Aj} \alpha_j V_{jk} \alpha_k + \dots \right] E_q,$$

where

$$V_{ij} = -U_{ij} e^{-i\vec{q} \cdot (\vec{x}_i - \vec{x}_j)}$$

is dependent on \vec{q} . Let us introduce

$$\bar{S}_{ij} = V_{ij} \alpha_j + \sum_{k \neq A} V_{ik} \alpha_k V_{kj} \alpha_j + \dots \quad (17)$$

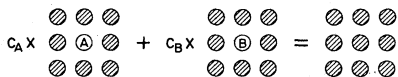


FIG. 4. A schematic representation of the equation which determines the “average” polarizability.

We then have

$$\begin{aligned} p_A &= \alpha_A \left[1 + \sum_j \bar{S}_{Aj} + \bar{S}_{AA} \sum_j \bar{S}_{Aj} \right. \\ &\quad \left. + \bar{S}_{AA}^2 \sum_j \bar{S}_{Aj} + \dots \right] E_q \\ &= \alpha_A \left[1 + \frac{1}{1 - \bar{S}_{AA}} \sum_j \bar{S}_{Aj} \right] E_q. \end{aligned} \quad (18)$$

Now introduce the sum

$$\begin{aligned} S_{ij} &= V_{ij} \alpha + \sum_k V_{ik} \alpha V_{kj} \alpha + \dots \\ &= [V\alpha + (V\alpha)^2 + \dots]_{ij} = \left[\frac{V\alpha}{1 - V\alpha} \right]_{ij}. \end{aligned} \quad (19)$$

We can then write ($j \neq A$)

$$\begin{aligned} S_{Aj} &= \bar{S}_{Aj} + \bar{S}_{AA} \frac{\alpha}{\alpha_A} \bar{S}_{Aj} + \bar{S}_{AA} \frac{\alpha}{\alpha_A} \bar{S}_{AA} \frac{\alpha}{\alpha_A} \bar{S}_{Aj} + \dots \\ &= \bar{S}_{Aj} \frac{1}{1 - \bar{S}_{AA} \alpha / \alpha_A} \end{aligned} \quad (20)$$

and

$$\begin{aligned} S_{AA} &= \bar{S}_{AA} \frac{\alpha}{\alpha_A} + \left[\bar{S}_{AA} \frac{\alpha}{\alpha_A} \right]^2 + \dots \\ &= \bar{S}_{AA} \frac{\alpha}{\alpha_A} (1 + S_{AA}) \end{aligned}$$

or

$$\bar{S}_{AA} = \frac{S_{AA}}{1 + S_{AA}} \frac{\alpha_A}{\alpha}. \quad (21)$$

Equations (20) and (21) give

$$\bar{S}_{Aj} = \frac{S_{Aj}}{1 + S_{AA}} \quad (j \neq A). \quad (22)$$

Substituting Eqs. (21) and (22) into Eq. (18) gives

$$p_A = \alpha_A \frac{1 + \sum_j S_{Aj}}{1 + S_{AA} (1 - \alpha_A / \alpha)} E_q.$$

But according to Eq. (19) we have

$$\begin{aligned} S_{AA} &= \left[\frac{V\alpha}{1 - V\alpha} \right]_{AA} \equiv \langle A | \frac{V\alpha}{1 - V\alpha} | A \rangle \\ &= \sum_q |\langle A | \vec{q} \rangle|^2 \frac{\tilde{V}(\vec{q})\alpha}{1 - \tilde{V}(\vec{q})\alpha} = \frac{1}{N} \sum_q \frac{\tilde{V}(\vec{q})\alpha}{1 - \tilde{V}(\vec{q})\alpha}, \end{aligned}$$

where (we are using the bra-ket vector notation)

$$\langle i | \vec{q} \rangle = \frac{1}{\sqrt{N}} e^{i\vec{q} \cdot \vec{x}_i} .$$

since

Furthermore,

$$\begin{aligned} \sum_j S_{Aj} &= \sum \langle A | \hat{S} | j \rangle = \sum_{qj} \langle A | \vec{q} \rangle \langle \vec{q} | j \rangle \tilde{S}(\vec{q}) \\ &= \sqrt{N} \sum_q \langle A | \vec{q} \rangle \delta_{q0} \tilde{S}(\vec{q}) = \tilde{S}(0) \end{aligned}$$

$$\sum_j \langle \vec{q} | j \rangle = \frac{1}{\sqrt{N}} \sum_j e^{-i\vec{q} \cdot \vec{x}_j} = \delta_{q0} \sqrt{N} .$$

We get now

$$\begin{aligned} p_A &= \alpha_A \frac{1 + \tilde{V}(0)\alpha/[1 - \tilde{V}(0)\alpha]}{1 + (\alpha - \alpha_A)(1/\mathcal{A}^*) \int d^2q' \tilde{V}(\vec{q}')/[1 - \alpha\tilde{V}(\vec{q}')] } E_q \\ &= \frac{1}{1 + \alpha\tilde{U}(\vec{q})} \frac{\alpha_A}{1 + (\alpha - \alpha_A)(1/\mathcal{A}^*) \int d^2q' \tilde{U}(q + q')/[1 + \alpha\tilde{U}(q + q')] } E_q . \end{aligned} \quad (23)$$

We find an analogous expression for p_B if $\alpha_A \rightarrow \alpha_B$. Finally we must calculate the rhs of Eq. (16), but this was done already in Sec. II [see Eq. (4)],

$$p = \frac{\alpha}{1 + \alpha\tilde{U}(\vec{q})} E_q \equiv \alpha_0(\vec{q}, \omega) E_q . \quad (24)$$

For the general case when we have M different types of molecules on the metal surface we can write down the analog to Eq. (16) [note that since $\tilde{U}(\vec{q})$ has the same periodicity as the reciprocal lattice, we can replace $\vec{q} + \vec{q}' \rightarrow \vec{q}'$ in the integral occurring in Eq. (23)],

$$\sum_{\mu=1}^M \frac{c_\mu \alpha_\mu}{1 + (\alpha_\mu - \alpha)(1/\mathcal{A}^*) \int_{\text{BZ}} d^2q \tilde{U}(\vec{q})/[1 + \alpha\tilde{U}(\vec{q})]} = \alpha , \quad (25)$$

and the total polarizability can be expressed in α as

$$\alpha_0(\vec{q}, \omega) = \frac{\alpha(\omega)}{1 + \alpha(\omega)\tilde{U}(\vec{q})} . \quad (26)$$

In IRS we are, of course, only interested of the $\vec{q}=0$ component of $\alpha_0(\vec{q}, \omega)$, but we have given the derivation above for a general \vec{q} so that it also applies to EELS [see Eq. (2)]. The integral occurring in Eq. (25) was evaluated in Sec. II. Notice that Eq. (25) must be solved for α by iteration. If the zero-order solution is taken as $\alpha = \sum_\mu c_\mu \alpha_\mu$, then it turns out that about 10 iterations are necessary. Finally, we notice that if we have a monolayer of one single adsorbed molecule A ($c_A = 1$) then Eq. (25) is satisfied by $\alpha = \alpha_A$ and Eq. (26) reduces to Eq. (4), which is an exact result.

IV. NUMERICAL RESULTS FOR A SUBSTITUTIONALLY DISORDERED MONOLAYER

The expression for $\alpha_0(\vec{q}, \omega)$ derived in Sec. III has such a complicated structure that very little information can be gained through an analytical study. In this section we therefore present numeri-

cal results obtained from Eqs. (1), (13), (25), and (26). The calculations are for isotopic mixtures of the molecules $A = {}^{12}\text{C}^{16}\text{O}$ and $B = {}^{12}\text{C}^{18}\text{O}$ adsorbed on Cu(100). For this system we have used

$$\begin{aligned} \alpha_e &= 3 \text{ \AA}^3, \quad \alpha_v = 0.27 \text{ \AA}^3, \quad \tilde{U}(0) = 0.3 \text{ \AA}^{-3}, \\ \omega_A &= 2043 \text{ cm}^{-1}, \quad \omega_B = 1996 \text{ cm}^{-1}, \end{aligned}$$

where the electronic polarizability α_e and vibrational polarizability α_v are chosen to give the best possible agreement with experiment, as discussed in Sec. VI. For convenience, we henceforth express ω in wave numbers (cm^{-1}).

We start by giving an elementary and somewhat rough picture of the structure of $\Delta(\omega)$. Assume first that there is no interaction between the adsorbed molecules, i.e., $U_{ij} = 0$. According to Eqs. (25) and (26) we can then write the polarizability as $\alpha_0 = c_A \alpha_A + c_B \alpha_B$. If the damping γ , occurring in the expressions for α_A and α_B [see Eq. (5)], is infinitesimally small then from Eq. (1)

$$\Delta(\omega) \sim c_A \omega_A^2 \delta(\omega - \omega_A) + c_B \omega_B^2 \delta(\omega - \omega_B) .$$

$\Delta(\omega)$ should be a sum of two δ functions centered at the frequencies ω_A and ω_B and having weights (if $\omega_A \approx \omega_B$) c_A and c_B proportional to the concen-

tration of the respective species, as shown in Fig. 5(a). Suppose now that $U_{ij} \neq 0$ so that the molecules interact with each other. The integral in Eq. (25) will then, in general, have a finite imaginary part, i.e., α_0 will be complex. This implies that $\Delta(\omega)$ will be nonvanishing for finite intervals of ω and not just at the two frequencies ω_A and ω_B , as when $U_{ij} = 0$. The physical reason for this is quite obvious if we notice that the adsorbed molecules may be considered as a distribution of variably sized clusters of type A and B molecules. Each cluster will have slightly different eigenfrequencies due to the interaction U_{ij} between the molecules. Thus we get a distribution of absorption peaks which for an infinite system will merge into a continuous absorption band as shown schematically in Fig. 5(b). The integrated intensity of the two peaks for the noninteracting system ($U_{ij} = 0$) is, as we have already pointed out, proportional to the concentrations c_A and c_B of the respective species. This means that the total integrated intensity is independent of composition. For the interacting system ($U_{ij} \neq 0$) a large amount of intensity is removed from the low-frequency peak to the high-frequency peak. In fact, the spectrum in Fig. 5(c) is calculated with $c_A = 0.1$, $c_B = 0.9$, and the damping $\gamma = 3 \text{ cm}^{-1}$. The total integrated intensity must even for the interacting system be independent of composition.

Let us assume that we have a mixture of A and B molecules with $c_A = 0.1$ and $c_B = 0.9$ and that the damping $\gamma = 0$. Figure 6(a) shows the absorption spectrum $\Delta(\omega)$ calculated from Eqs. (1), (13), (25), and (26). We notice that $\Delta(\omega)$ has two singularities with tails to the left. These singularities are weaker than δ functions and are smeared out completely when a finite damping is introduced [Fig. 5(c)]. Within the CPA all molecules of the same type, say A , vibrate in the same way, i.e., the induced dipole moment $p_A(t)$ is the same function of time for all A molecules. In fact, we have in Eq. (23) given an explicit expression for p_A . Figures 6(b) and 6(c) show the amplitude and phase (relative to the external electric field) of p_A and p_B :

$$p_A(t) = |p_A| e^{-i\omega t + i\Psi_A},$$

$$p_B(t) = |p_B| e^{-i\omega t + i\Psi_B}.$$

We notice the following remarkable results: The amplitude $|p_A|$ is *much* larger than $|p_B|$ for nearly all ω . Furthermore, at the lower peak $\Psi_A \approx -90^\circ$, i.e., $p_A E^* \approx -i |p_A E^*|$. Since we can write

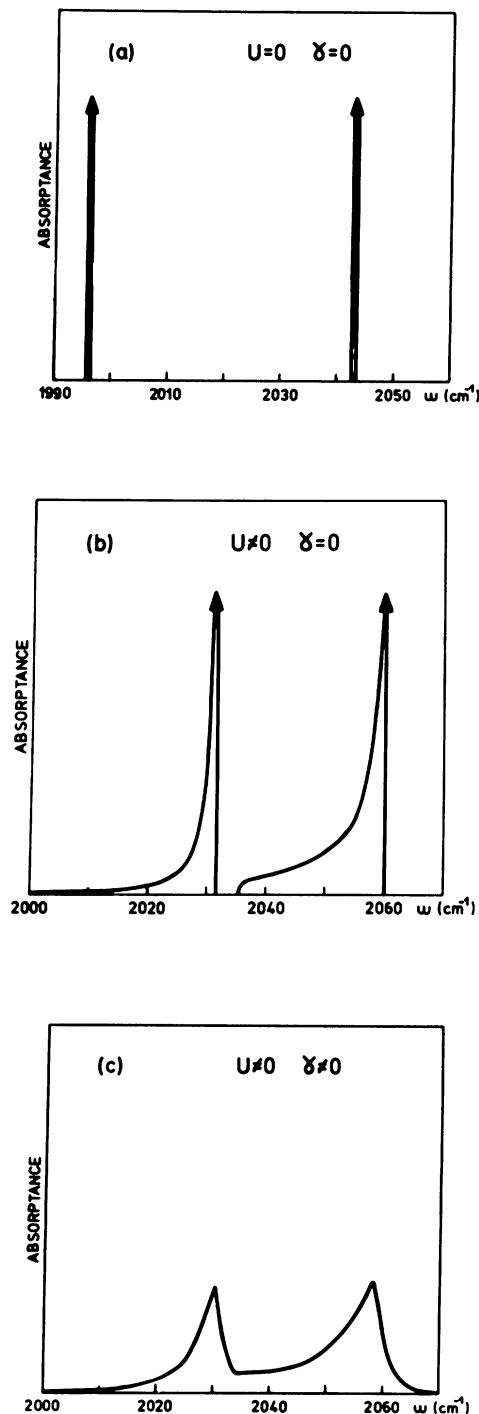


FIG. 5. The IR-absorption spectra [i.e., $\Delta(\omega)$] for a mixture of $A = {}^{12}\text{C}^{16}\text{O}$ and $B = {}^{12}\text{C}^{18}\text{O}$ molecules with $c_A = 0.1$ and $c_B = 0.9$. (a) Noninteracting molecules ($U_{ij} = 0$) with undamped vibrations ($\gamma = 0$). (b) Dipole-dipole interacting molecules ($U_{ij} \neq 0$) with undamped vibrations ($\gamma = 0$). (c) Dipole-dipole interacting molecules ($U_{ij} \neq 0$) with damped vibrations ($\gamma = 3 \text{ cm}^{-1}$).

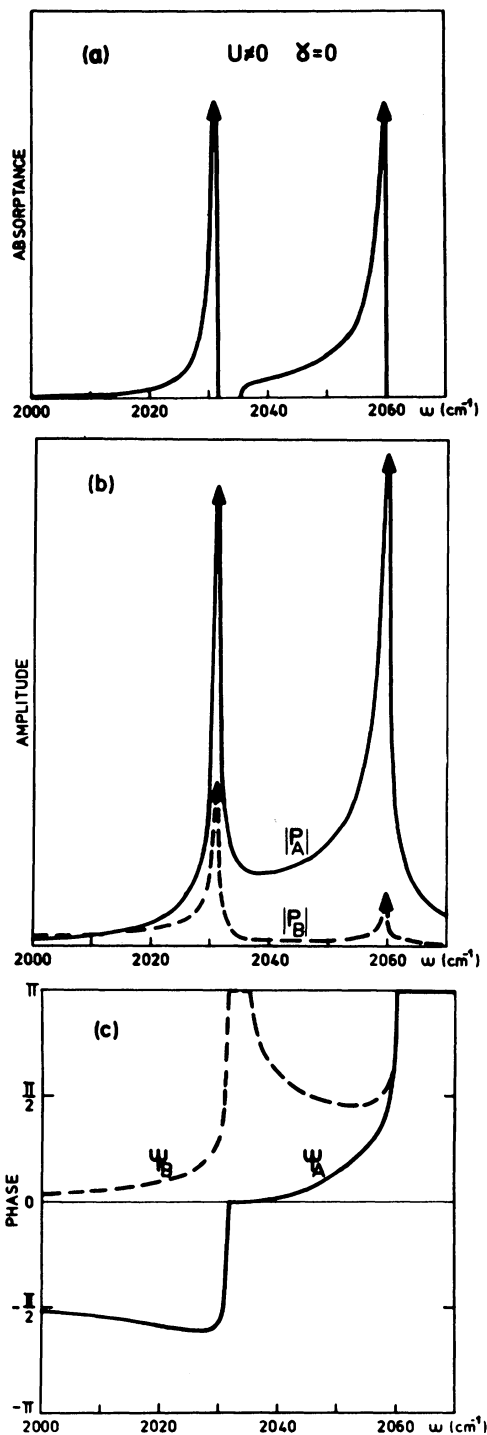


FIG. 6. Spectra for a mixture of $A = {}^{12}\text{C}^{16}\text{O}$ and $B = {}^{12}\text{C}^{18}\text{O}$ molecules with $c_A = 0.1$ and $c_B = 0.9$. Dipole-dipole interaction ($U_{ij} \neq 0$) with undamped vibrations ($\gamma = 0$). (a) The absorption spectrum $\Delta(\omega)$. (b) The vibration amplitudes $|p_A|$ and $|p_B|$. (c) The phases Ψ_A and Ψ_B of $p_A(t)$ and $p_B(t)$, respectively, relative to the external electric field $E(t)$.

$$\Delta(\omega) \sim c_A \text{Im} p_A E^* + c_B \text{Im} p_B E^* \quad (27)$$

it follows that A molecules give a negative contribution to $\Delta(\omega)$. Physically this means that the A molecules radiate *more* electromagnetic field energy into space than they absorb from the external field. Due to energy conservation, this is possible only if the A molecules receive a net amount of energy from the B molecules due to the interaction U_{ij} . We may then visualize the basic process taking place at the lower absorption peak as follows: Suppose that an incident photon is absorbed by a B molecule, which is likely since 90% are B molecules. Due to the interaction U_{ij} the excitation jumps between the molecules, until it arrives at an A molecule where it most probably is radiated back into space. This process will drain intensity from the low-frequency peak.

The asymmetry in the intensity of the two absorption bands, as a function of mixture, can also be understood as follows: Since the A molecules have a higher resonance frequency than the B molecules, the A molecules can screen the electric field at the metal surface for frequencies in the lower absorption band (and consequently reduce the absorbance) while the B molecules cannot do this for frequencies in the upper absorption band.

As can be seen from Fig. 6(a), just above the low-frequency absorption peak there is a narrow frequency interval where $\Delta(\omega) = 0$. This does not mean that the molecules are not vibrating at these frequencies [on the contrary according to Fig. 6(b)] but only that they vibrate in phase (molecules A) or 180° out of phase (molecules B) so that both terms in Eq. (27) are zero. This also happens above the high-frequency absorption peak, where both A and B molecules vibrate 180° out of phase [Fig. 6(c)]. At the high-frequency absorption peak both A and B molecules vibrate with phases $0 < \Psi < \pi$ and therefore give positive contributions to $\Delta(\omega)$. Note also that even if $c_A \ll c_B$ the A molecules will give a contribution to $\Delta(\omega)$ which is at least as large as the contribution from the B molecules because of the very large difference in vibrational amplitudes.

The discussion above has been carried out with the damping $\gamma = 0$. For the finite γ we expect all the sharp structure in Figs. 6(a)–6(c) to be smeared out. Figure 7 shows the absorption spectra calculated from the CPA expression for several different mixtures with a damping γ corresponding to peak width [full width at half maximum (FWHM)] of 3 cm^{-1} .

We would like to emphasize that the discussion above is valid not only for isotopic mixtures but

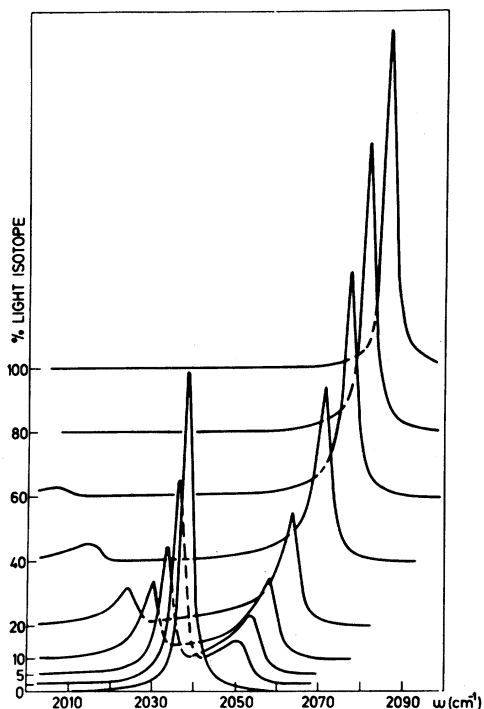


FIG. 7. The absorption spectra $\Delta(\omega)$ for different mixtures of $A = {}^{12}\text{C}^{16}\text{O}$ and $B = {}^{12}\text{C}^{18}\text{O}$ with a damping $\gamma = 3 \text{ cm}^{-1}$.

also for mixtures of different kinds of molecules (e.g., CO and N_2) or even for one kind of molecule simultaneously adsorbed in two different positions (e.g., on top and in bridge) on the same surface. How strong the coupling and resulting redistribution of intensity depends on how large the frequency difference $\Delta\omega = \omega_A - \omega_B$ ($\omega_A > \omega_B$) is compared with the bandwidth of the modes $\Omega_A(q)$ and $\Omega_B(q)$ of monolayers of A and B molecules. The bandwidth $\Delta\Omega_A$ of a monolayer of A molecules can be derived from Eq. (8) and is roughly $\Delta\Omega_A \sim \omega_A \alpha_v \tilde{U}(0) / 2[1 + \alpha_e \tilde{U}(0)]$ as long as $\alpha_v \tilde{U}(0) \ll 1$. For example, for $c(2 \times 2)\text{CO}/\text{Cu}(100)$ we get $\Delta\Omega \approx 50 \text{ cm}^{-1}$. If $\Delta\omega \lesssim \Delta\Omega$ then the A and B vibrational modes will couple strongly and the behavior of $\Delta(\omega)$ will be as discussed above. However, even if $\Delta\omega$ would be several times larger than $\Delta\omega$, it is not possible to neglect the coupling between the two modes when discussing the intensity in the lower absorption band when $c_A \gg c_B$. Furthermore, the electronic polarizability of all the adsorbed molecules must always be taken into account, independent of how large $\Delta\omega$ is, when calculating the intensities in both the upper and lower absorption bands.

V. NUMERICAL RESULTS FOR AN INCOMPLETE MONOLAYER

In this section we apply the theory from Sec. III to a discussion of the absorption spectra of an incomplete monolayer of CO adsorbed on Cu(100). We assume that the CO molecules are randomly distributed among the sites of the $c(2 \times 2)$ Bravais net, i.e., we have a substitutionally disordered monolayer consisting of

$$A = {}^{12}\text{C}^{16}\text{O} \text{ and } B = \text{“vacuum.”}$$

Consider now $c_A = 0.5$, i.e., that half of the sites are occupied. Using

$$\alpha_e = 3 \text{ \AA}^3, \quad \alpha_v = 0.27 \text{ \AA}^3, \quad \tilde{U}(0) = 0.3 \text{ \AA}^{-3}, \\ \omega_A = 2043 \text{ cm}^{-1}$$

from the previous section, Fig. 8 shows the absorption spectra calculated from the CPA expression (26) with $\gamma = 0$ and $\gamma = 3 \text{ cm}^{-1}$. The width of the peak in Fig. 8(b) is 4 cm^{-1} , so there is an extra broadening of about 1 cm^{-1} due to disorder. The center frequency of the absorption peak (2074 cm^{-1}) is about 31 cm^{-1} above ω_A (2043 cm^{-1}) and 12 cm^{-1} below the full monolayer frequency (2086 cm^{-1}). Mahan and Lucas⁷ have derived the following expression for the center frequency Ω as a function of coverage c_A ,

$$\left(\frac{\Omega}{\omega_A} \right)^2 = 1 + \frac{c_A \alpha_v \tilde{U}(0)}{1 + c_A \alpha_e \tilde{U}(0)} \quad (28)$$

which in the present case ($c_A = 0.5$) gives $\Omega - \omega_A = 28 \text{ cm}^{-1}$. This is about 10% smaller than the prediction of the more exact CPA theory.

Figure 9 shows the amplitude p_A and phase Ψ_A of the induced dipole moment. These quantities have been obtained from Eq. (23) with $\gamma = 0$. We notice that the molecules vibrate nearly in phase ($\Psi_A \approx 0$) below and exactly 180° out of phase above the center frequency of the absorption peak.

This behavior is similar to that of a single harmonic oscillator in an external field. For $\gamma = 0$ the phase of such a system has a step transition from $\Psi = 0$ to $\Psi = \pi$ and an absorption peak in the form of a Dirac δ function. Due to the disorder of the incomplete monolayer these sharp features are smoothed somewhat, giving a low-frequency absorption tail and weakening the peak singularity.

Figure 10 shows the absorption spectra $\Delta(\omega)$ for different coverages of ${}^{12}\text{C}^{16}\text{O}$ calculated from the CPA expression with $\gamma = 3 \text{ cm}^{-1}$. Note the continuous increase in peak width with decreasing coverage down to very low coverages. This is a

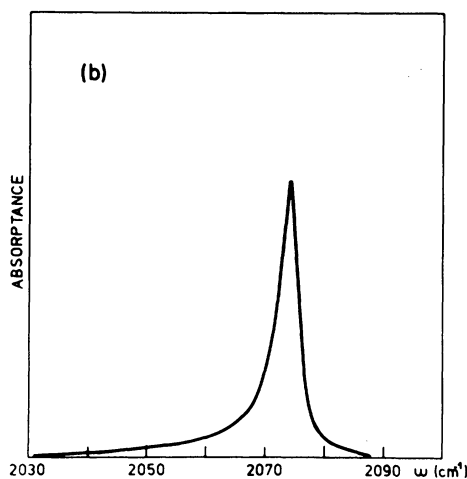
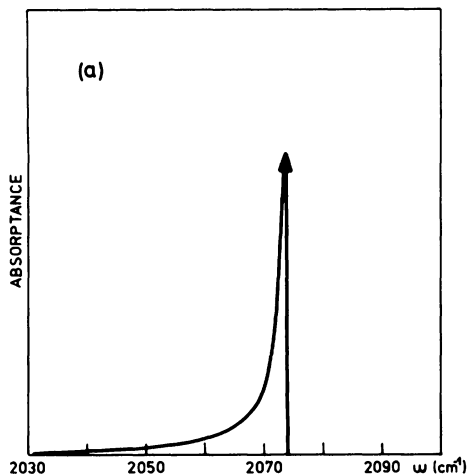


FIG. 8. The absorption spectra $\Delta(\omega)$ of an incomplete monolayer $A = {}^{12}\text{C}^{16}\text{O}$ with $c_A = 0.5$. (a) Undamped vibrations ($\gamma = 0$). (b) Damped vibrations ($\gamma = 3 \text{ cm}^{-1}$).

consequence of the long range of the dipole interaction. Figure 11 shows how the peak width (FWHM) varies with coverage when the damping γ is 3 cm^{-1} (curve A) and 9 cm^{-1} (curve B).

VI. ISOTOPIC MIXTURES OF CO ON Cu(100)

In this section we will show that there is a very good quantitative agreement between the theory developed above and experimental IRS data on iso-

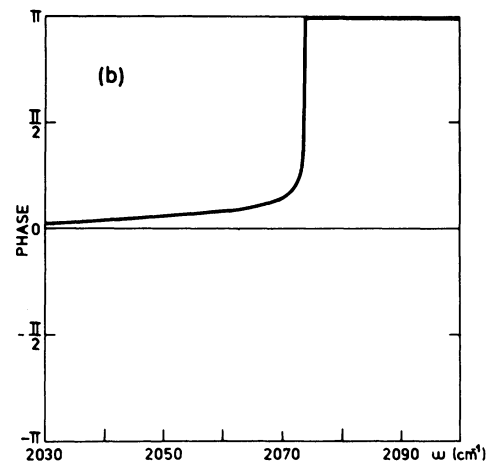
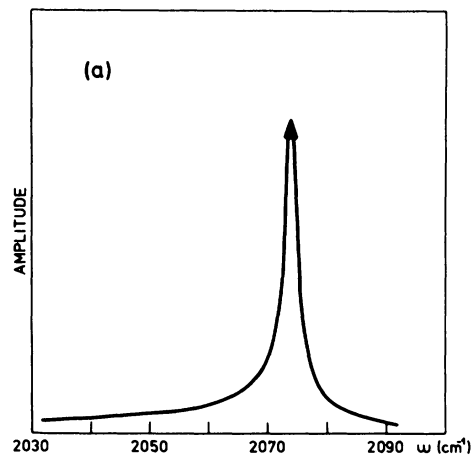


FIG. 9. An incomplete monolayer of $A = {}^{12}\text{C}^{16}\text{O}$ with $c_A = 0.5$ and $\gamma = 0$. (a) The vibration amplitude $|p_A|$. (b) The phase Ψ_A of $p_A(t)$ relative to the external electric field $E(t)$.

topic mixtures of CO on Cu(100). A detailed report on the experimental conditions and other properties of this system is given elsewhere.¹⁴ Here we only reproduce the results which are relevant for our present discussion. First we consider mixtures at full coverage of the $c(2 \times 2)$ structure. Figure 12 shows the experimental absorption spectra for several different mixtures of ${}^{12}\text{C}^{16}\text{O}/{}^{12}\text{C}^{18}\text{O}$. The properties of this system are summarized in Fig. 13. The solid lines in the figure are theoretical curves calculated from Eqs. (1), (25), and (26) with $A = {}^{12}\text{C}^{16}\text{O}$ and $B = {}^{12}\text{C}^{18}\text{O}$ and

$$\tilde{U}(0) = 0.3 \text{ \AA}^{-3},$$

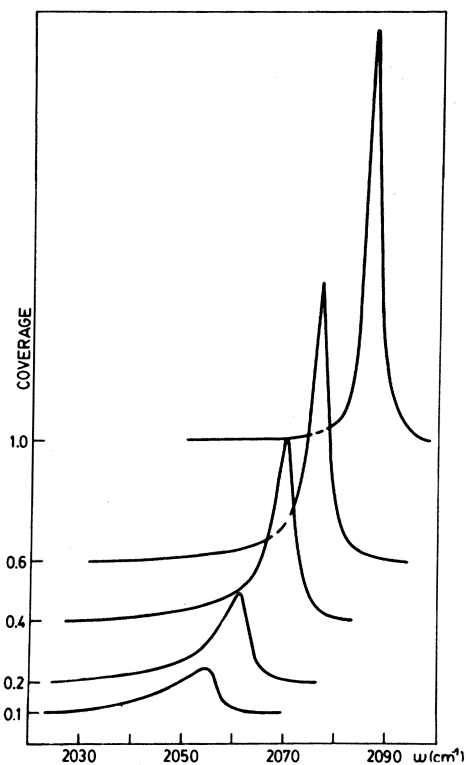


FIG. 10. The absorption spectra $\Delta(\omega)$ for different coverages of $A = {}^{12}\text{C}^{16}\text{O}$ with a damping $\gamma = 3 \text{ cm}^{-1}$.

$$\alpha_e = 3.0 \text{ \AA}^3,$$

$$\alpha_v = 0.27 \text{ \AA}^3,$$

$$\omega_A = 2043 \text{ cm}^{-1},$$

$$\omega_B = 1996 \text{ cm}^{-1},$$

as in Sec. III. The values of α_e and α_v used above were chosen to give the best possible fit between theory and experiment. There exists in principle an independent way of obtaining α_v , namely, from the total absorbance in IRS or the inelastic cross

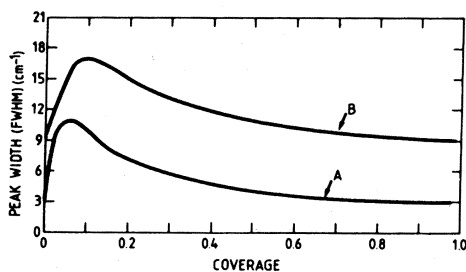


FIG. 11. The peak width (FWHM) for different coverages of ${}^{12}\text{C}^{16}\text{O}$ with a damping $\gamma = 3 \text{ cm}^{-1}$ (curve A) and $\gamma = 9 \text{ cm}^{-1}$ (curve B).

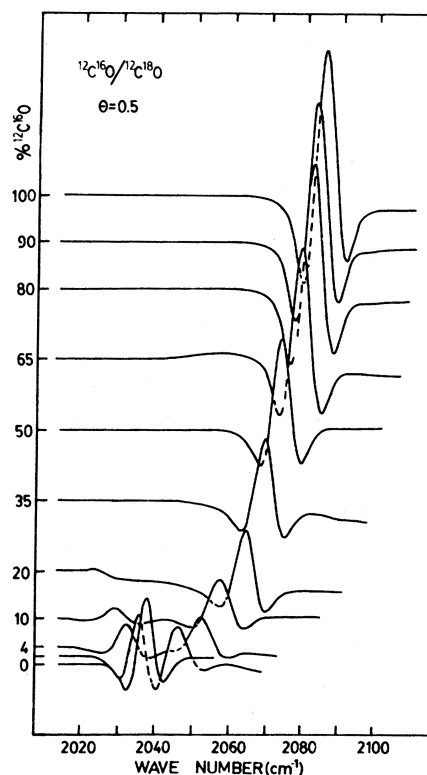


FIG. 12. Experimental IRS spectra for different compositions of ${}^{12}\text{C}^{16}\text{O}/{}^{12}\text{C}^{18}\text{O}$ on $\text{Cu}(100)$ at 100 K in the $c(2 \times 2)$ structure.

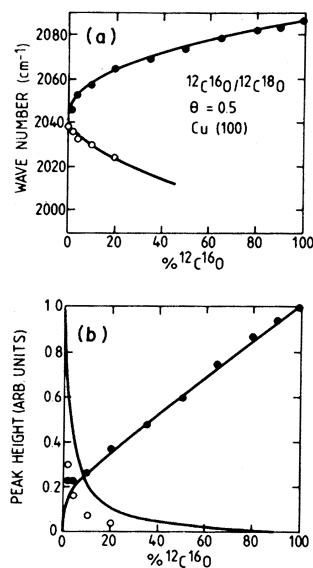


FIG. 13. Peak height and position of the absorption spectra of mixtures of ${}^{12}\text{C}^{16}\text{O}/{}^{12}\text{C}^{18}\text{O}$ in the $c(2 \times 2)$ structure on $\text{Cu}(100)$. The circles are experimental data while the solid lines are calculated from Eqs. (1), (25), and (26).

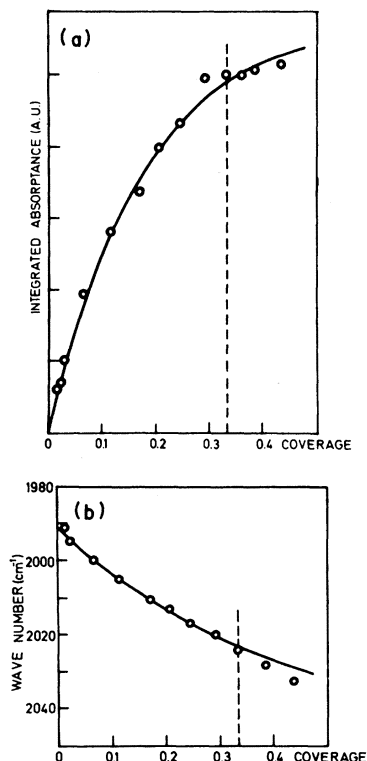


FIG. 14. The IR absorption of different coverages of CO on Ru(001). The circles are experimental data from Ref. 15 and the solid lines are given by Eqs. (29) and (30).

section in EELS and we shall come back to this in Sec. VIII.

A comment upon the broadening of the absorption peaks due to the substitutional disorder. In the calculated spectra shown in Fig. 7 one can see an increasing broadening of the high-frequency peak when the $^{12}\text{C}^{16}\text{O}$ concentration decreases. For a $c_A = 0.5$ mixture the peak width has increased with about 1 cm^{-1} , which is in good agreement with what we find experimentally.¹⁴

VII. COVERAGE DEPENDENCE OF CO ON Cu(100) and Ru(001)

We have measured the absorbance of incomplete monolayers of $^{12}\text{C}^{16}\text{O}$ adsorbed on Cu(100). The main result is a positive frequency shift of the C-O vibration from 2077 cm^{-1} at low coverage to 2086 cm^{-1} at the full $c(2 \times 2)$ structure, i.e., a total shift of 9 cm^{-1} .

This is not in accordance to the predictions of the CPA theory, since the calculations in Sec. V

show that the shift is expected to be from the frequency of one adsorbed molecule 2043 cm^{-1} to the full monolayer frequency 2086 cm^{-1} , i.e., a total shift of 43 cm^{-1} . As pointed out by Hollins and Pritchard,³ there are two possible explanations for this observation; either there is clustering in the incomplete monolayer or the metal-CO chemisorption bond changes with coverage.

However, as will be discussed elsewhere¹⁴ it seems unlikely that clustering occurs for CO on Cu(100). This is also in agreement with the findings on Cu(111).³ Consequently, this indicates that for CO on Cu(100) there exists a downward chemical shift from zero to full coverage of about 30 cm^{-1} .

It is now interesting to compare these results with measurements of CO adsorbed on a transition metal. IRS data for CO adsorbed on Ru(001) has been reported by Pfnür *et al.*¹⁵

In Fig. 14 we reproduce their results for the center frequency and integrated absorbance as a function of coverage. A full ordered structure corresponds to a coverage of 0.33. The solid lines are theoretical curves calculated from the simplified version of the CPA theory as described in Appendix B:

$$\left[\frac{\Omega}{\omega_A} \right]^2 = 1 + \frac{c_A \alpha_v \tilde{U}(0)}{1 + c_A \alpha_e \tilde{U}(0)}, \quad (29)$$

$$\int d\omega \Delta(\omega) \sim \frac{c_A \alpha_v \tilde{U}(0)}{[1 + c_A \alpha_e \tilde{U}(0)]^2}. \quad (30)$$

Notice that the screening, due to the electronic polarizability α_e , reduces both the frequency shift $\Omega - \omega_A$ and the integrated absorbance $\int d\omega \Delta(\omega)$. In fact, if $\alpha_e = 0$ both of these quantities would be approximately linear in c_A in marked contrast to the experimental results shown in the figure. In the two equations above we have used

$$\alpha_e = 2.8 \text{ \AA}^3, \quad \alpha_v = 0.28 \text{ \AA}^3,$$

$$\tilde{U}(0) = 0.17 \text{ \AA}^{-3}, \quad \omega_A = 1991 \text{ cm}^{-1}.$$

$\tilde{U}(0)$ was calculated for the relevant structure and α_e and α_v have been chosen to give the best possible agreement between theory and experiment.

To summarize, we have found satisfactory agreement between theory and experiment for incomplete monolayers of CO adsorbed on Ru(001), while the dipole-dipole coupling alone cannot explain the behavior on Cu(100). This is in accor-

dance with the observation that whereas CO adsorbed on transition metals generally exhibits a rather large (40 cm^{-1}) positive frequency shift (as expected from the dipole-dipole coupling), this is not the case on noble metals. In fact, CO adsorbed on Ag, Au, and even on Cu(111) exhibits *negative* frequency shifts.³

VIII. THE DYNAMICAL DIPOLE MOMENT OF CHEMISORBED MOLECULES

A useful quantity, which can be obtained from an IRS or EELS experiment, is the vibrational polarizability α_v as defined by Eq. (5). α_v can be related to the matrix element $\langle b | \vec{\mu} | a \rangle$ of the dipole moment operator between the ground state $|a\rangle$ and the vibrational excited state $|b\rangle$ through

$$\alpha_v = \frac{2 |\langle b | \vec{\mu} | a \rangle|^2}{\hbar\omega_A} \quad (31)$$

$\mu = |\langle b | \vec{\mu} | a \rangle|$ is often called the dynamical dipole moment of the transition $|a\rangle \rightarrow |b\rangle$. In this section we will make some scattered comments about the dynamical dipole moment of the C-O stretch vibration of chemisorbed CO. Our discussion will necessarily be less precise than in the earlier sections.

By comparing theory with experiment for the isotopic mixtures in Sec. VI we found that $\alpha_v \approx 0.27 \text{ \AA}^3$ for CO adsorbed on Cu(100). Since $\hbar\omega_A \approx 0.26 \text{ eV}$ it follows from Eq. (31) that $\mu \approx 0.25 \text{ D}$.¹⁶ However, there exists in principle an independent way of obtaining α_v (if α_e is known), namely, from the integrated absorptance in IRS or the inelastic scattering cross section in EELS. The value of α_v for CO adsorbed on Cu(100) that is previously given in the literature¹⁷ (0.06 \AA^3) must, in the light of the derivation of Eq. (9) in Sec. II, be reinterpreted to mean

$$\frac{\alpha_v}{[1 + \alpha_e \tilde{U}(0)]^2} = 0.06 \text{ \AA}^3.$$

Using this equation with $\tilde{U}(0) = 0.3 \text{ \AA}^{-3}$ and $\alpha_e = 3 \text{ \AA}^3$ as above one obtains $\alpha_v = 0.23 \text{ \AA}^3$. Even if this is rather close to the value determined from the isotopic mixtures, there exists a considerable spread in the reported values of the vibrational polarizabilities from IRS and EELS.

A gas phase CO molecule has $\mu = 0.1 \text{ D}$ but one would expect an increased dynamical dipole moment for a chemisorbed molecule from the following arguments¹⁸: Upon chemisorption electrons

from the CO 5σ orbitals are donated to the metal while metal electrons are back donated into the CO $2\pi^*$ orbitals. Since $2\pi^*$ is antibonding, the CO frequency is expected to decrease, which is in agreement with experiment. Stretching the C-O bond lowers the $2\pi^*$ level causing charge to flow from the metal to the CO and giving rise to a large dynamical dipole moment.

It is known that the vibrational frequency¹⁹ and the electronic structure²⁰ are rather similar for CO adsorbed on a transition metal and bonded in the corresponding metal carbonyl. It is therefore interesting to compare the dynamical dipole moments for the C-O vibration of two such systems. From EELS studies of CO on Ni(100) one can derive $\mu = 0.25 \text{ D}$ which should be compared with the dynamical dipole moment $\mu = 0.24 \text{ D}$ obtained from IRS measurements on Ni(CO)₄ (Ref. 19). A second mechanism which has been proposed to cause an increased dynamical dipole moment upon chemisorption is the so-called "self-image enhancement." However, as is shown in Appendix C, this mechanism can only explain a small fraction of the increase in μ .

Consequently, the main part of the increase in the dynamical dipole moment is caused by charge oscillations between the metal and the molecule. Due to the continuous energy spectrum of a metal, such charge oscillations cannot take place adiabatically, i.e., some energy inevitably must be lost through excitation of electron hole pairs in the metal. In fact, it has been shown within a simple model calculation²¹ that the vibrationally excited molecule has a lifetime τ given approximately by

$$\frac{1}{\tau} = 2\pi\Omega(\delta n)^2,$$

where Ω is the vibration frequency and δn is the charge oscillation between the molecule and the metal. From the knowledge of the increase in the dynamical dipole moment upon chemisorption one can estimate δn and therefore also the lifetime τ . Such an estimate has been made²¹ and the result is in reasonable agreement with the experimentally determined lifetime.¹⁴

IX. PHOTOSYNTHESIS

In this section we shall discuss briefly an interesting application of the theory of Sec. III to a fundamental step in photosynthesis. We do not intend to give a quantitative calculation but only to point out that a model used in the literature may

be rather crude or even incorrect.

What we will discuss is the first step in photosynthesis,²² schematically shown in Fig. 15. In the cells of green plants there exist plane "sheets" (lipid-protein interfaces) on which a monolayer of a mixture of several different kinds of chlorophyll molecules is located.²³ The most important of these is chlorophyll *a*. The distance between two nearby chlorophyll molecules in the monolayer is about 10 Å. Since they have a huge dynamical dipole moment (typically 6 D, among the largest observed in nature) associated with electronic excitations, it follows that if one of the chlorophyll molecules is optically excited by absorption of a photon, then the excited molecule will couple strongly to the other molecules via a dipole-dipole interaction. Consequently, the excitation will not be localized to one molecule alone but it will jump between the chlorophyll molecules in exactly the same way as do the vibrational excitations in an isotopic mixture as discussed earlier. However, if the excitation arrives at a particular chlorophyll molecule, denoted by *E* in Fig. 15, then it will be trapped and transferred to an enzyme in a way which is not known in detail. The enzyme will then use the energy thus obtained to produce carbohydrates from H₂O and CO₂. From experimental observations it is known that the concentration of the *E* molecules (the so-called active centers) is very low—only about 0.3%.

We think that the model used in Sec. III can be applied also to a discussion of the optical properties of this chlorophyll molecule monolayer. Only a few trivial changes of the theory are required. The chlorophyll molecules are not located on a metal vacuum interface as are the CO molecules, but on a protein-lipid interface. This means that the dielectric screening by the surrounding media will be changed, but in an obvious way. Furthermore, in order for the excitation to be trapped when it arrives at an active center, the damping (occurring in the expression for the polarizability α_E) of an *E* molecule, must be rather large (γ_E

must be chosen to reproduce the mean time the excitation stays at an *E* molecule before it is transferred into the enzyme). The damping γ of the other chlorophyll molecules will then be much smaller, i.e., $\gamma \ll \gamma_E$.

In some treatments found in the literature, one has simply used a random walk (often only taking into account jumps between nearest-neighbor molecules) to describe the propagation of an excitation in the chlorophyll monolayer. But we know that such an approach fails completely when applied to the isotopic mixtures and there is no reason to expect it to work better for a chlorophyll molecule mixture. The most striking effect of the infrared properties of isotopic mixtures is that mixing a host of heavy isotope *B* with only a few percent of a light isotope *A* ($\omega_A > \omega_B$) completely changes the absorption spectra by transfer of intensity from the low-frequency peak to the high-frequency peak. A more detailed study shows, moreover, that the amplitude of the *A* molecules for nearly all frequencies is *much* larger than for the *B* molecules. Consequently, if the *A* and *B* vibrations both have the same damping γ , then an *A* molecule dissipates *much* more energy per unit time than a *B* molecule.

Now, suppose that the discussion above also applies to the optical absorption spectrum of the chlorophyll molecule mixture. More precisely, assume that the *E* molecule has an absorption band slightly above the absorption bands of the other chlorophyll molecules. Then, when a photon is absorbed by the monolayer, we expect the probability of finding the excitation at an "active" molecule to be much larger than the probability that the excitation is at any other particular chlorophyll molecule. Stated in another way, the excitation will on the average make rather few jumps (much less than what would follow from a random walk) before it arrives at an *E* molecule. This is important for the efficiency of photosynthesis, since there always exists the possibility that an excitation, during its travel towards an *E* molecule, gets lost by spontaneous emission of light (fluorescence) or by internal conversion (these processes are taken into account by the damping γ).

To sum up, the discussion above implies that the high efficiency of photosynthesis may partly be due to the *E* molecule having an absorption band slightly *above* the absorption bands of the other molecules. This conclusion is in direct contradiction to what is found in the literature on this subject.²²

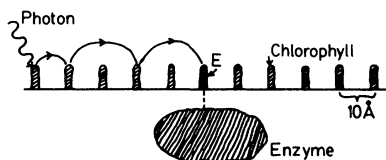


FIG. 15. A schematic picture of the first step in photosynthesis.

X. SUMMARY AND CONCLUSIONS

In this work we have used the CPA to interpret measured IRS spectra of substitutionally disordered monolayers consisting of mixtures of different CO isotopes adsorbed on a Cu(100) surface. The basic assumption was that the molecules interact with each other only through a dipole-dipole interaction. The very good agreement between theory and experiment for these isotopic mixtures proves that the dipole-dipole interaction is the dominating vibrational coupling mechanism for the stretch vibration of CO molecules adsorbed on Cu and probably on any other metal.

We also showed that in interpreting the integrated absorbance in IRS, or the relative loss intensity in EELS, it is necessary to take into account the screening due to the electronic polarizability of the adsorbed molecules.

Furthermore, a simplified version of the CPA was used for a discussion of the absorption spectra of incomplete monolayers of a single isotope on the assumption that the CO molecules were randomly distributed. Comparison between theory and experiment indicates that the dipole-dipole interaction alone is responsible for the coverage dependent frequency shift for CO adsorbed on a transition metal [Ru(001)], whereas there is a nearly equally large counteracting chemical shift on a noble metal [Cu(100)].

Next we discussed the meaning and origin of the dynamical dipole moment of adsorbed CO molecules. We found that the increase of the dynamical dipole moment (by a factor 2–3) upon adsorption is probably due to charge oscillations between the CO $2\pi^*$ MO and the metal and not, as recently has been proposed by several authors, due to the so-called self-image enhancement.

Finally, we outlined how the developed theory can be applied to a fundamental step in photosynthesis.

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APPENDIX A

Here we give a proof of Eq. (1). Consider a metal surface with adsorbed molecules. Let $\hat{\mu}_i$ be the

dipole moment operator of the molecule at \vec{x}_i . The interaction energy between an external electric field \vec{E}_i and the molecules is given by

$$H' = - \sum_i \hat{\mu}_i \cdot \vec{E}(\vec{x}_i, t). \quad (\text{A1})$$

The external electric field \vec{E} at the metal surface can be written as²⁴

$$\vec{E}(\vec{x}, t) = \vec{n} \vec{n} \cdot \vec{e} \frac{1}{2} E_0 (1+g) e^{i(\vec{k}_{\parallel} \cdot \vec{x}_{\parallel} - \omega t)} + \text{c.c.}, \quad (\text{A2})$$

where \vec{n} is a unit vector normal to the metal surface, g is the reflection factor of p -polarized light, and \vec{e} is the polarization vector of the incident light. The rate w at which the molecules absorb light can be calculated from the golden rule formula with H' as the perturbation:

$$w = \frac{2\pi}{\hbar^2} \sum_b |\langle b | H' | a \rangle|^2 \delta(\omega - \omega_{ba}), \quad (\text{A3})$$

where $|a\rangle$ is the ground state and $|b\rangle$ is an excited state of the monolayer. Equations (A1), (A2), and (A3) give

$$w = \frac{2N}{\hbar} E_0^2 (\vec{n} \cdot \vec{e})^2 \left| \frac{1+g}{2} \right|^2 \text{Im}\alpha(0, \omega),$$

where

$$\text{Im}\alpha(\vec{q}, \omega) = \frac{1}{N} \frac{\pi}{\hbar} \sum_b \left| \sum_i \langle b | \hat{\mu}_i | a \rangle \times e^{i\vec{q} \cdot \vec{x}_i} \right|^2 \delta(\omega - \omega_{ba})$$

is the imaginary part of the polarizability of the monolayer. We can relate w to the change in reflectance $\Delta(\omega)$ as²⁴

$$\Delta(\omega) = \frac{8\pi}{c} \frac{w \hbar \omega}{A E_0^2 |g|^2}$$

and so

$$\Delta(\omega) = \frac{16\pi}{c} \frac{N}{A} \omega G(\theta) \text{Im}\alpha(0, \omega),$$

where

$$G(\theta) = \frac{\sin^2 \theta}{\cos \theta} \left| \frac{\sqrt{\epsilon} \cos \theta}{\sqrt{\epsilon} \cos \theta - 1} \right|^2$$

is a function of the angle of incidence θ and the dielectric function ϵ of the metal [$G(\theta)$ is discussed in Ref. 24].

APPENDIX B

The CPA result for $\Delta(\omega)$ is rather complicated and it would therefore be useful if one could find a reasonable, accurate approximation for $\Delta(\omega)$. For isotopic mixtures we have not been able to find such an approximation. However, for incomplete monolayers of one single isotope A one can obtain a rather simple approximation for $\Delta(\omega)$, which for some purposes is accurate enough, as follows. We perform an ensemble average (denoted by a bar) on Eq. (15):

$$\bar{p}_i = \bar{\alpha}_i E_i + \sum_j (-U_{ij}) \overline{\alpha_i \alpha_j} E_j + \dots \quad (\text{B1})$$

Now, let us denote $\bar{\alpha}_i = c_A \alpha_A \equiv \bar{\alpha}$. Within the so-called "average T -matrix approximation" one writes

$$\overline{\alpha_i \alpha_j} = \bar{\alpha}^2, \quad \overline{\alpha_i \alpha_j \alpha_k} = \bar{\alpha}^3, \dots$$

Equation (A4) will then be a geometric series in $X = \bar{\alpha} \sum_j U_{ij}$:

$$\bar{p}_i = \bar{\alpha} E_0 (1 + X + X^2 + \dots) = \frac{\bar{\alpha} E_0}{1 - X}$$

and so [note: $\tilde{U}(0) = \sum_i U_{ij}$]

$$\alpha_0(\omega) = \frac{\bar{\alpha}}{1 + \bar{\alpha} \tilde{U}(0)}$$

From this equation and Eq. (1) one can calculate $\Delta(\omega)$ and get the result given in Sec. VII.

APPENDIX C

Let α_v^0 and α_e^0 be the vibrational and electronic polarizabilities of a gas phase CO molecule and let α_v and α_e denote the same quantities for an adsorbed molecule. Now, if self-image enhancement were the only source for the increased polarizability of an adsorbed molecule, then in the simplest description, where the molecule is treated as a point dipole located at a distance d above the image plane, one has

$$p = \alpha^0 \left[E_0 + \frac{p}{4d^3} \right] = \alpha E_0.$$

Here E_0 is an external electric field which induces a dipole p in the molecule. From the equation above one gets

$$\alpha = \frac{\alpha^0}{1 - \alpha^0/4d^3}.$$

Using this equation one can prove that

$$\alpha_v = \alpha_v^0 \cdot \frac{1 + (\alpha_e - \alpha_e^0)/\alpha_e}{1 - (\alpha_e - \alpha_e^0)(\alpha_e^0 + \alpha_v^0)/\alpha_e \alpha_e^0}. \quad (\text{C1})$$

For CO adsorbed on Cu(100) we have found that $\alpha_e \approx 3 \text{ \AA}^3$ and with $\alpha_e^0 \approx 2.7 \text{ \AA}^3$ and $\alpha_v^0 \approx 0.05 \text{ \AA}^3$ one gets from Eq. (A5) $\alpha_v \approx 1.2\alpha_v^0$, while we find experimentally $\alpha_v \approx 4\alpha_v^0$. Consequently, we conclude that if the slight increase in the electronic polarizability which is observed upon chemisorption is due to self-image enhancement then only a few percent of the huge increase of the vibrational polarizability can be caused by the same mechanism.

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