# Tunable Fermi resonance in a C<sub>2</sub>F<sub>6</sub> monolayer on graphite

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The infrared absorption spectrum of  $C_2F_6$  physisorbed on graphite in the commensurate 2×2 phase has two strong, narrow peaks associated with the  $\nu_5$  molecular vibration. They are interpreted as a Fermi resonance between  $\nu_5$  and the  $\nu_8 + \nu_{11}$  combination band, which are shifted into near-coincidence by dynamic dipole coupling between the adsorbate molecules. The splitting and relative strengths have been measured as the coupling is reduced in a lower-density, tilted, incommensurate phase and are consistent with theory. It is shown that two alternative descriptions, as Fermi resonance between exciton modes of the layer or as dynamic dipole coupling between molecules with two vibration modes, are essentially equivalent. To fit the experimental frequency shifts and absolute absorption strengths, it is necessary to use a value for the  $\nu_5$  vibrational polarizability of the adsorbed molecule that is somewhat smaller than the value for the free molecule. © 2002 American Institute of Physics. [DOI: 10.1063/1.1462611]

#### I. INTRODUCTION

Infrared reflection absorption spectroscopy (IRRAS) is widely used to study chemisorbed molecular layers on metals,<sup>1,2</sup> but only occasionally has it been applied to physisorbed films on graphite.<sup>3-5</sup> Graphite is a sufficiently good conductor in the infrared so the usual dipole selection rule applies: Only the projection of the induced dipole moment perpendicular to the surface is observable in infrared absorption. For a molecule such as  $C_2F_6$ , which has a strong absorption band  $(\nu_5)$  with dipole moment parallel to the C–C axis and another  $(\nu_7)$  perpendicular, IRRAS provides a rather direct experimental measure of the average tilt of molecules with respect to the surface normal.<sup>6</sup> Apart from applications, IRRAS study of adsorbates on graphite offers an opportunity to observe dynamic dipole coupling effects with minimal complication from chemical shifts, which are comparable in magnitude in most chemisorption systems.

Knorr and co-workers studied C2F6 monolayers on graphite by x-ray diffraction<sup>7,8</sup> and heat capacity<sup>7</sup> measurements. They identified a low temperature, triangular commensurate  $2 \times 2$  phase, with molecules inferred to be upright, and a phase transition to an expanded triangular phase (TI) at higher temperatures and lower chemical potentials (lower spreading pressure). The x-ray data show a continuous expansion on moving away from the commensurate phase. Our IRRAS data show that, in addition, the molecular C-C axis becomes tilted progressively from nearly perpendicular to the surface at the transition to nearly parallel to the surface some distance away. This work will be reported in detail elsewhere.<sup>9</sup> Two samples of the absorption spectrum in the region of  $\nu_5$  for the commensurate monolayer are shown by dashed curves in Fig. 1. This spectrum hardly changes over the entire commensurate region of the phase diagram. There are two sharp peaks of nearly equal height at 1132.8 and 1142.8 cm<sup>-1</sup>, each only slightly wider than the instrumental resolution (after apodization) of 0.75 cm<sup>-1</sup>. The 3D gasphase  $\nu_5$  band is visible at lower energy, with its Q branch at 1117 cm<sup>-1</sup>. Figure 2 shows the shifts of the two frequencies in the TI phase on moving away from the commensurate phase (points at the upper right end) by reducing the 3D pressure; hence, the chemical potential. Data for four temperatures fall on nearly the same curve.

The  $\nu_5$  mode is nondegenerate and all adsorbate sites are equivalent for the proposed triangular monolayer structure. Therefore, the splitting of the absorption band is attributed to mixing with the  $v_8 + v_{11}$  combination band. In the gas phase this band is centered at  $1139 \text{ cm}^{-1}$  and it has integrated absorbance about 1/20 that of  $\nu_5$ . It has suitable symmetry  $(E_u \times E_g = E_u + A_{1u} + A_{2u}$  for the symmetry group  $D_{3d}$  of the free molecule) to mix with  $\nu_5$  ( $A_{2u}$ ). In the surface monolayer, the strong  $\nu_5$  mode is expected to be shifted to higher frequency by dynamic dipole coupling.<sup>10,11</sup> That is, each vibrating molecule sees the electric dipole fields produced by its vibrating neighbors; this couples the individual molecular vibrations into a band. Infrared wavelengths are much longer than the intermolecular spacing, and so couple only to vibrational "excitons" at the center of the Brillouin zone (that is, with all molecules vibrating in phase). The effect is treated classically. If the dipole axes are oriented perpendicular to the layer, the effect is to shift the zone-center exciton to higher frequency.<sup>10</sup> The spectra in Fig. 1 suggest that dynamic dipole coupling has shifted the  $\nu_5$  mode sufficiently that, in the absence of anharmonic coupling, it would nearly coincide with the combination mode. Then, anharmonic coupling (Fermi resonance) produces strong level mixing and repulsion of about  $\pm 5 \text{ cm}^{-1}$ . (On the surface, the symmetry of the molecule oriented perpendicular to the surface is reduced to  $C_{3v}$ , representing the loss of inversion symmetry; this does not change the mixing of the combination mode with  $\nu_5$ .) In the following sections the experiment is described, the theory is reviewed, and its predictions compared with the experimental results.

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FIG. 1. Monolayer absorption spectra in the  $\nu_5$  region of  $C_2F_6$ . The two dashed curves are in the commensurate phase of the monolayer. The three solid curves are at lower pressures in the tilted incommensurate phase. Absorption by the 3D gas is centered at 1117 cm<sup>-1</sup>.

#### **II. EXPERIMENT**

The substrate is a slab of highly oriented pyrolytic graphic clamped to a copper cold finger, cooled by a closed-cycle refrigerator.<sup>12</sup> This is enclosed in a small cell, with ZnSe windows oriented for 70° angle of incidence, which is maintained at a temperature only slightly higher than that of



FIG. 2. Frequency of the upper peak vs frequency of the lower peak for various pressures at four different temperatures. Points at the upper right are in the commensurate phase. The line represents theory, with parameters from the fit shown in Fig. 3.



FIG. 3. (a) Separation of the peaks in Fig. 1 vs frequency of the lower peak. (b) Relative area under the peaks in Fig. 1. The lines are theory, described in the text.

the substrate. In these measurements the adsorbate is in equilibrium with 3D  $C_2F_6$  gas admitted to the cell. The outer vacuum jacket of the cryostat has another pair of ZnSe windows. Spectra were taken with a Mattson Research Series Fourier transform spectrometer at 0.5 cm<sup>-1</sup> nominal resolution, summing scans for about 3 min per spectrum. The rather unconventional cryogenic arrangement has several advantages, among them that measurements can be extended to relatively high pressures and substrate contamination problems are reduced by the cold cell walls.

## **III. RESULTS**

Five spectra at 105 K for different gas pressures are shown in Fig. 1. At this temperature the monolayer TI phase is crossed in a convenient range of pressures, high enough to ensure rapid equilibration but low enough to avoid excessive absorption by the 3D gas. Antireflection coating of our windows was optimized for a higher frequency range, so fringes are a problem in the range around  $\nu_5$ . In order to remove them without reducing resolution, a background spectrum was constructed by splicing together segments away from peaks of two other spectra, not included in the figure. This background was subtracted from each spectrum shown.

The three spectra in the TI phase are shown by solid lines. As the pressure is reduced, both peaks move to lower frequency and broaden. The higher-frequency peak loses strength relative to the lower peak. At the same time the surface  $\nu_7$  peak near 1275 cm<sup>-1</sup> (not shown) has appeared and is increasing in strength, indicating that the molecules are tilting away from the surface normal. The peak frequencies and the areas under the bands in Fig. 1 were measured and the results are plotted in Fig. 3. Figure 3(a) shows the separation between the two peaks as a function of the lower frequency. Figure 3(b) shows the ratio of the peak areas as a function of the lower frequency. The lines are results of theory discussed below. Here, we simply note that there are

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two relevant free parameters and both curves are completely determined by fitting each to the highest frequency data point.

## **IV. ANALYSIS**

Fermi resonance occurs when a fundamental vibrational mode is close in frequency to an overtone or combination mode. The latter exist by virtue of anharmonic terms in the Hamiltonian of the form  $A_{1122}q_1^2q_2^2$  or  $A_{123}q_1q_2q_3$ , where  $q_i$ are vibrational normal coordinates in the harmonic approximation (and 1=2 in the case of an overtone). A term of the cubic type involves a third mode and contributes only in second-order or higher of perturbation theory because it is odd in at least one coordinate. Thus, the contribution to the energy is of the form  $|\langle \psi_{12}|A_{123}q_1q_2q_3|\psi_3\rangle|^2/(E_1+E_2)$  $-E_3$ ), where  $\psi$ 's are harmonic wave functions and  $E_i$  are first-order energies.<sup>13–15</sup> If  $E_1 + E_2 \cong E_3$  the energy denominator approaches zero and the perturbation treatment is not valid. Instead, it is necessary to choose new linear combinations of the (nearly) degenerate basis states to diagonalize the relevant part of the Hamiltonian. This procedure results in a fractional admixture of  $\psi_3$  in the new eigenstates, given by<sup>16</sup>

$$a_{\pm} = \sqrt{\frac{1}{2} \pm \frac{\delta}{2\sqrt{\delta^2 + 4W^2}}},\tag{1}$$

where  $\delta = E_3 - E_{12}$ ,  $E_{12} = (E_1 + E_2)$  and  $W^2 = |A_{123}|^2$ . The new energy eigenvalues are

$$\nu_{\pm} = \frac{1}{2} (E_3 + E_{12}) \pm \frac{1}{2} \sqrt{\delta^2 + 4W^2}.$$
 (2)

If  $E_3$  is considered variable, Eqs. (1) and (2) describe anticrossing behavior, in which the larger admixture of  $\psi_3$  is transferred from the lower-energy branch to the higherenergy branch as  $E_3$  increases through the value  $E_{12}$ . In the case where the combination mode 1+2 has no oscillator strength except that derived by mixing with the fundamental mode 3, the absorption strength associated with each mode will be proportional to  $a_{\pm}^2$ . If the molecules are condensed on a surface, interactions with the substrate and interactions between the adsorbate molecules will shift these vibrational frequencies. The latter interaction is predominantly from dynamic dipole coupling, which will shift  $E_3$  as a function of adsorbate density.

A Fermi resonance situation in an adsorbed film can be treated from two points of view, both of which are instructive. The starting point is a set of molecules with harmonic vibration modes, perturbed by anharmonic corrections within the molecule and by linear interactions between the molecules. The first approach (the "Fermi resonance approach") treats the linear interactions first, constructing Bloch waves of coupled vibrations or "excitons," then treats the principal anharmonic term by the Fermi method.<sup>17</sup> This leads to Eqs. (1) and (2) above. Note that, besides  $E_3$ , this theory contains two parameters ( $E_1 + E_2$ ) and  $W^2$ . The second approach (the "dynamic dipole coupling" approach) treats the perturbations in the reverse order: A combination mode of the free molecule, with frequency and polarizability which would result from treatment of the anharmonic perturbations, is in-

cluded along with the fundamental mode in the starting point of a dynamic dipole coupling calculation. This calculation is carried through in some detail next.

Dynamic dipole coupling is treated by a classical meanfield model. The polarization on site i is

$$p_i = \alpha(\omega)(E_0 + E_i),$$

where  $\alpha(\omega)$  is the molecular polarizability,  $E_0$  is the external electric field (assumed to be uniform over distances much larger than the lattice spacing), and  $E_i$  is the field at site *i* due to the polarization of all of the other molecules and their images in the surface

$$E_i = -\sum_{j(\neq i)} U_{ij} p_j \,.$$

If all sites are equivalent, these combine to give

$$p = \frac{\alpha(\omega)}{1 + U\alpha(\omega)} E_0 = \alpha_0(\omega) E_0, \qquad (3)$$

where  $U = \sum_{j(\neq i)} U_{ij}$  is the dipole sum and  $\alpha_0(\omega)$  is the polarizability per molecule of the monolayer. For molecules with *N* relevant vibrational modes

$$\alpha(\omega) = \alpha_e + \sum_{n=1}^{N} \frac{\alpha_n \omega_n^2}{\omega_n^2 - \omega^2 - i \gamma_n \omega_n \omega},$$
(4)

where  $\alpha_e$  is the electronic polarizability. We will assume the damping  $\gamma_n$  is negligible. This polarizability function has *N* pairs of poles at  $\pm \omega_n$  and, provided  $\alpha_e$  is nonzero, *N* pairs of zeros. The transformation of  $\alpha(\omega)$  into  $\alpha_0(\omega)$  by the interaction *U* can be rewritten from Eq. (3) as

$$\frac{1}{\alpha_0(\omega)} = U + \frac{1}{\alpha(\omega)}.$$
(5)

It is evident that  $\alpha_0(\omega)$  must have the same analytic form as Eq. (4) for  $\alpha(\omega)$ , but with different parameters  $\overline{\alpha}_e(U)$ ,  $\overline{\alpha}_n(U)$ ,  $\overline{\omega}_n(U)$ . The poles, but not the zeros, are shifted. One more general property of the transformation is evident from inspection of Eq. (5): If the interaction is separated into two parts,  $U = U_2 + U_1$ , two successive transformations with  $U_1$ and  $U_2$  are equivalent to a single transformation with U. For example,  $U_1$  might be the interaction of a molecule with its own image;<sup>18</sup> or for tilted molecules  $U_1$  and  $U_2$  might be the in-plane and perpendicular components of the field, projected on the molecular axis. For any starting point  $\alpha_e$ ,  $\alpha_n$ ,  $\omega_n$ , in the 2N+1 dimensional parameter space, varying Ugenerates a trajector that is the same for any starting point on that trajectory. Thus, the empirical input parameters have no fundamental significance in the theory.

Consider first the case of a single resonance, N=1. Equations (3) and (4) give

$$\bar{\omega}_1^2 = \omega_1^2 (1 + U\alpha_1 / (1 + U\alpha_e)), \tag{6a}$$

$$\bar{\alpha}_{\rho} = \alpha_{\rho} (1 + U\alpha_{\rho})^{-1}, \tag{6b}$$

and

$$\bar{\alpha}_1 = \alpha_1 (1 + U\alpha_e)^{-1} (1 + U(\alpha_e + \alpha_1))^{-1}.$$
 (6c)

Two independent combinations of these should be invariant along the trajectory and can serve to label the trajectory. These can be taken as  $\overline{\omega}_1^2 \overline{\alpha}_1 / \overline{\alpha}_e^2$  and  $\overline{\alpha}_e(\overline{\alpha}_2 + \overline{\alpha}_1) / \overline{\alpha}_1$ . With these fixed, any noninvariant parameter (say,  $\overline{\omega}_1$  or  $\overline{\alpha}_1$ ) can serve to designate the location along the trajectory. The area under the absorption peak is proportional to  $\overline{A}_1$  $= n \int \omega \operatorname{Im} \{\alpha_0(\omega)\} d\omega$ , where *n* is the number of molecules per unit area.<sup>10</sup> Provided  $\gamma_1 \ll 1$ , this can be written as  $\overline{A}_1$  $= \pi n \overline{\omega}_1 \overline{R}_1$ , where  $\overline{R}_1$  is the residue at the pole at  $+\overline{\omega}_1$  of  $\alpha_0(\omega)$ . Using the residue evaluated with Eq. (4) for U=0, this is  $A_1 = (\pi/2)n \alpha_1 \omega_1^2$ . This transforms as  $\overline{A}_1 = A_1/(1 + \alpha_e)^2$ , in agreement with Persson and Ryberg.<sup>10</sup> The recurring factor  $(1 + U\alpha_e)^{-1}$  represents the screening of the field at the site of one molecule due to the electronic polarizability of all of the other molecules and the images.

For N=2 the analogous relations are slightly more complicated. In the following one can choose (or not) to identify resonance 1 with a fundamental mode and resonance 2 with a combination mode. The poles of  $\alpha_0(\omega)$  are found to be

$$\bar{\omega}_{1,2}^2 = \frac{1}{2}(\Omega_1^2 + \Omega_2^2) \pm \frac{1}{2}\sqrt{(\Omega_1^2 - \Omega_2^2)^2 + Y^2},\tag{7}$$

where

$$\Omega_1^2 = \Omega_2^2 + Kx, \tag{8a}$$

$$\Omega_2^2 = \omega_1^2 \omega_2^2 (\alpha_1 + \alpha_2) / K,$$
 (8b)

$$K = \alpha_1 \omega_1^2 + \alpha_2 \omega_2^2, \tag{9}$$

$$x = \overline{U} - Q, \tag{10a}$$

$$\bar{U} = U/(1 + U\alpha_e), \tag{10b}$$

$$Q = (\omega_2^2 - \omega_1^2)(\alpha_1 \omega_1^2 - \alpha_2 \omega_2^2)/K^2,$$
(11)

and

$$Y^{2} = 4 \alpha_{1} \alpha_{2} \omega_{1}^{2} \omega_{2}^{2} (\omega_{2}^{2} - \omega_{1}^{2})^{2} / K^{2}.$$
 (12)

Equation (7) has the form of an avoided crossing with asymptotes  $\Omega_2^2$ , a constant, and  $\Omega_1^2(U)$ . The other input parameters are transformed as follows:

$$\bar{\alpha}_e = \alpha_e (1 + U\alpha_e)^{-1}, \tag{13}$$

as before;

$$\bar{K} = K(1 + U\alpha_e)^{-2}, \tag{14}$$

$$\bar{\alpha}_1 \bar{\omega}_1^2, \bar{\alpha}_2 \bar{\omega}_2^2 = \frac{1}{2} \bar{K} \frac{\sqrt{\Delta^2 + Y^2} \pm \Delta}{\sqrt{\Delta^2 + Y^2}},\tag{15}$$

with

$$\Delta = \Omega_2^2 - \Omega_1^2. \tag{16}$$

From this one can easily calculate  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$ . The quantities  $\bar{\Omega}_2^2$ ,  $\bar{Y}^2$ , and  $\bar{K}/\bar{\alpha}_e^2$  are invariants. The areas under the two absorption peaks are proportional to the two quantities in Eq. (15).

In order to compare the results of the Fermi resonance approach with the results of the dynamic dipole approach, it is necessary to square Eq. (2)

$$\nu_{\pm}^{2} = \frac{1}{2}(E_{3}^{2} + E_{12}^{2}) + W^{2}$$
$$\pm \frac{1}{2}\sqrt{(E_{3}^{2} - E_{12}^{2})^{2} + 4W^{2}(E_{3} + E_{12})^{2}}.$$
(17)

Typically W is not more than a few percent of  $E_{12}$ , so it is a good approximation to neglect the additive term  $W^2$ . Then,

Eq. (17) is nearly equivalent to Eq. (7) with the identification  $E_{12}=\Omega_2$  and  $E_3=\Omega_1$ , and  $W^2=Y^2/16\Omega_2^2$ . A shortcoming of this identification is that the presence of  $E_3$  multiplying  $W^2$  under the radical skews the crossover region slightly. This is corrected by the modified identification  $E_{12}=\sqrt{\Omega_2^2+W^2}$  and  $E_3=\sqrt{\Omega_1^2-3W^2}$ , for which the equivalence of the two equations is exact to order  $W^2$ .

The normalized absorption strengths are found from Eq. (15)

$$\bar{A}_{1,2}/(A_1 + A_2) = \frac{1}{2} \pm \frac{1}{2} \frac{\Delta}{\sqrt{\Delta^2 + Y^2}}.$$
(18)

In the Fermi resonance approach, the absorption strengths are proportional to the square of the admixture coefficient a in Eq. (1)

$$a_{\pm}^{2} = \frac{1}{2} \pm \frac{1}{2} \frac{\delta}{\sqrt{\delta^{2} + W^{2}}}.$$
(19)

Multiplying the numerator and denominator by  $E_{12}+E_3$  gives

$$\bar{A}_{1,2}/(A_1 + A_2) = a_{\pm}^2$$

$$= \frac{1}{2} \pm \frac{1}{2} \frac{E_3^2 - E_{12}^2}{\sqrt{(E_3^2 - E_{12}^2)^2 + 4W^2(E_3 + E_{12})^2}}.$$
 (20)

With either identification, this differs from Eq. (18) by a term of order  $W^2$ . This difference is at most barely discernible in Fig. 3(b).

Da Costa and Coleman<sup>19</sup> have calculated the IRRAS spectrum for a multilayer film with two Lorentzian resonances, treating the film as a continuum layer with Fresnel reflection at the interfaces. In this model the absorption peaks correspond to the LO modes, that is, the zeros of the dielectric function. This corresponds to the limit  $U \rightarrow \infty$  in the 2D dynamic dipole calculation.

## V. DISCUSSION AND CONCLUSIONS

Essentially equivalent predictions for the frequencies of the coupled modes are obtained from the Fermi resonance approach, Eq. (2) or (17), and the dynamic dipole approach, Eq. (7), provided appropriate identifications are made of the parameters specifying the uncoupled mode energies and the coupling strength. Essentially the same expression for the relative strengths of the coupled modes is obtained, with the additional assumption in the Fermi resonance approach that the polarizability of the combination mode is derived entirely from mixing with the one resonant fundamental mode. The reason the dynamic dipole approach implies this constraint can be rationalized as follows: No other strongly mixing fundamental is included in the theory, so all other contributions to the polarizability of the combination mode are secondorder perturbations that are not contained in a linear response theory.

Other parameters such as the absolute strengths, Eq. (15), can be included in the Fermi resonance approach with further elaboration. The polarizability assigned to the fundamental mode in the Fermi resonance approach must be

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$$\alpha_1' = \alpha_1 + \alpha_2 \omega_2^2 / \omega_1^2, \tag{21}$$

in order that the total integrated area of the absorption peaks in each approach be the same. This is for the singleton. If the parameters of the single resonance transform under the dynamic dipole interaction according to Eq. (6) for N=1, the equivalence of areas is maintained for any U. The unperturbed frequency  $E_3$  is identified with  $\bar{\omega}_1$  of the N=1 calculation. Then, Eq. (6a) gives

$$E_3^2 = \omega_1^2 + \frac{\alpha_1' \omega_1^2}{1 + U \alpha_e} U.$$
 (22)

With Eq. (21), this has the same dependence on U as  $\Omega_1^2$ , confirming the consistency of the identification of  $E_3^2$  with  $\Omega_1^2$  (or with  $\Omega_1^2 - 3W^2$ ).

The experimental frequency splitting and relative intensities shown in Fig. 3 are fit with either theory by choosing  $W=5.0 \text{ cm}^{-1}$  to fit the theoretical minimum separation to the points at the right end of Fig. 3(a) and choosing  $E_{12}$  (or  $\Omega_2$ )=1132.5 cm<sup>-1</sup> to fit the frequency scale to the highest points in Fig. 3(b). This two-parameter fit is consistent with the whole data set. Note that these parameters are independent of  $\alpha_1$  (for fixed ratio  $\alpha_1/\alpha_2$ ) as well as of  $\alpha_e$  and U. Those three parameters will produce translation along the curves, i.e., affect the value of  $\Omega_1$ .

It is of interest to check the consistency of the value  $W = 5.0 \text{ cm}^{-1}$  with the gas-phase properties. Using also  $\delta = -22 \text{ cm}^{-1}$ , Eq. (1) predicts that  $(a_+/a_-)^2 = 0.047$ , which is consistent with the observed relative absorption strength of the combination mode if it is derived predominantly from mixing with  $v_5$ . Equation (2) predicts that the combination mode will be shifted upward from  $E_{12}(=v_8+v_{11})$  by 1.1 cm<sup>-1</sup>. The experimental estimates are  $v_8 = 522 \text{ cm}^{-1}$  (infrared<sup>20</sup>) and  $v_{11} = 619 \text{ cm}^{-1}$  (gas phase Raman<sup>21</sup>). This corresponds to a *downward* shift of about 2 cm<sup>-1</sup>. However, the precision of the data, particularly for the Raman transition, may be inadequate for a valid comparison.

One can ask whether the known parameters of the  $C_2F_6$ molecule and the dipole sum U for the commensurate monolayer are consistent with putting the system just beyond the crossing of the asymptotes, as is observed experimentally. For a triangular adsorbate lattice, U depends only on the lattice constant  $r_s$  (=4.92 Å for the 2×2 commensurate lattice) and the distance d of the dipoles above the image plane. The estimate  $d=2.8\pm0.4$  Å gives U=0.0919+0.0005/-0.0015. The mean electronic polarizability calculated from the gas refractivity is  $\alpha_e = 4.8 \text{ Å}^3$ . With an estimated value  $\gamma = 0.75 \text{ A}^3$  for the polarizability anisotropy, this gives  $\alpha_e$ = 5.3  $Å^3$  parallel to the molecular axis. The vibrational polarizability for mode  $\nu_5$ , calculated<sup>22,23</sup> from the absorption band strength<sup>24</sup> is  $\alpha_1 = 0.92$  Å<sup>3</sup>. (Earlier absorption data<sup>20</sup> give a value of 0.76 Å<sup>3</sup>.) These numbers give too large a value for  $\Omega_1$ . In order to fit the experimental points for the commensurate phase, U or  $\alpha_e$  must be changed by implausible amounts or the vibrational polarizability must be reduced to  $\alpha_1 = 0.55 \text{ Å}^3$ . [More precisely it is the combination  $\alpha_1 U$ , Eq. (10b), which must be reduced by a factor of 0.60.] The absolute absorption strength is proportional to K. The predicted integrated absorption strength in the commensurate phase, using the above parameters and the nominal angle of incidence of  $70^{\circ}$ , is  $0.120 \text{ cm}^{-1}$ . The measured value is 0.075 $cm^{-1}$ , smaller by a factor of 0.63. Equations (14) and (9) show that  $\overline{K}$ , like  $\alpha_1 \overline{U}$ , is effectively proportional to  $\alpha_1$ , but has twice as strong dependence on  $\alpha_e$  and opposite dependence on U. A chemical shift of  $\omega_1$  relative to  $\omega_2$  would also shift  $\Omega_1$ , but an implausible value (-14 cm<sup>-1</sup>) is required and it would have negligible effect on  $\overline{K}$ . This leaves reduction of  $\alpha_1$  the most plausible remedy. The origin of this apparent reduction in  $\alpha_1$  is not understood. It is not unique to mode  $\nu_5$ : A correction factor of about 0.75 must be applied to the frequency shift of the  $\nu_7$  mode in the most expanded solid monolayer phase, where the molecular axes are very nearly parallel to the surface. Calibrated absolute adsorption data are not available in this region. In chemisorption systems the vibrational polarizability can be modified substantially by static and dynamic charge exchange with the surface. This is not expected to be important in physisorption.

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