

Determination of twodimensional crystal structures by infrared spectroscopy

Otto Berg and George Ewing

Citation: *Journal of Vacuum Science & Technology A* **8**, 2653 (1990); doi: 10.1116/1.576688

View online: <http://dx.doi.org/10.1116/1.576688>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvsta/8/3?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

[Two-dimensional infrared spectroscopy of a structured liquid: Neat formamide](#)

J. Chem. Phys. **130**, 204518 (2009); 10.1063/1.3139002

[The molecular structure and orientation of antiferroelectric liquid crystal using the density-functional theory and two-dimensional correlation-polarized infrared spectroscopy](#)

J. Chem. Phys. **122**, 214913 (2005); 10.1063/1.1925270

[Peptide structure determination by two-dimensional infrared spectroscopy in the presence of homogeneous and inhomogeneous broadening](#)

J. Chem. Phys. **119**, 1569 (2003); 10.1063/1.1581853

[Polarized infrared spectroscopy and two-dimensional correlation spectroscopy study of molecular structure of ferroelectric liquid crystals with a naphthalene ring](#)

AIP Conf. Proc. **503**, 257 (2000); 10.1063/1.1306590

[A Machine for Synthesizing TwoDimensional Fourier Series in the Determination of Crystal Structures](#)

Rev. Sci. Instrum. **21**, 779 (1950); 10.1063/1.1745715



A PASSION FOR PERFECTION

PFEIFFER  VACUUM



HiCube® Eco turbopump station

■ \$4,995 for complete dry vacuum pump station

Are you looking for a perfect vacuum solution?
Please contact us!

Determination of two-dimensional crystal structures by infrared spectroscopy

Otto Berg and George Ewing^{a)}

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

(Received 21 August 1989; accepted 2 October 1989)

We have studied high-resolution infrared spectra of monolayers of small molecules on single-crystal NaCl (100). Vibrational features contain rich information on the structure and dynamics of the adsorbate array. Thanks to the relative passivity of the substrate, it is appropriate to describe the structure and vibrational motion of the monolayer as if it were a two-dimensional molecular crystal. The corresponding branch of symmetry theory involves 80 "plane groups." Plane-group analysis has been instrumental to our determination of nontrivial monolayer structures. The structure and spectroscopy of CO₂ on NaCl (100) will be discussed.

I. INTRODUCTION

The forces that cause adsorption to a dielectric surface are relatively weak. Molecules adsorbed through electrostatic and dispersion interactions retain their chemical identity; these perturbations are slight and well defined. Furthermore, these "physisorption" forces are in thermodynamic competition with interactions among adsorbates. Consequently, molecular adsorption can be an interesting intermediate between the physics of isolated molecules and the physics of bulk molecular solids.

Such considerations are relevant to our studies of the adsorption of small molecules to the surface of sodium chloride crystals. We observe internal vibrational resonances of physisorbed molecules. The multiplicity, intensity, shape, and polarization of these infrared absorbances provide detailed information about the adsorbate's local environment. In addition, the monolayers that we study are in equilibrium with the bulk gas. The layer forms a distinct phase, in which thermal processes guarantee an energetically preferred, and generally ordered, structure. Thus each species that we study presents a structural puzzle.

Our experience with carbon monoxide and carbon dioxide has justified cautious use of the "oriented gas" model for physisorption. This is the simplest possible interpretation of our spectroscopic data; it comprises two assumptions. First, it is assumed that the electronic properties of adsorbates are not altered. The integrated infrared cross section is taken from gas-phase measurements. Second, it is assumed that adsorbed molecules are locked in a specific orientation with respect to the surface. Adsorbed phase photometry and symmetry theory are straightforward in the oriented gas limit. When applied to spectra obtained under sufficiently constrained conditions, it is effective for the determination of monolayer structure. When used as the basis for theoretical calculations, the model reproduces salient features of the observed spectrum. In the following we demonstrate such an analysis for carbon dioxide adsorbed to the (100) face of sodium chloride. The range of applicability of this model is not known; its justification and limitations are detailed elsewhere.^{1,2}

Others have studied the CO₂/NaCl system using polycrystalline films^{3,4} and single crystals^{5,6} as substrates; heats of adsorption have been measured and calculated.⁷⁻⁹ These

researchers have shown that the adsorbed molecule's bond axis is not perpendicular to the surface. With the experimental and conceptual refinements discussed in this essay we can propose a specific structural model.

II. OBSERVATIONS

The adsorption substrate was prepared from a single-crystal boule of NaCl. It was cleaved in air to produce slabs with clean (100) faces exposed. Two such slabs were mounted in an ultrahigh vacuum chamber. The crystals were cooled, and an unsaturated pressure of CO₂ was maintained. The beam from a Fourier transform infrared (FTIR) spectrophotometer passed through the chamber and both crystals; thus four identical interfaces were probed, each tilted 60° from the direction of infrared propagation. A polarizer was used to select a specific component of the infrared beam for analysis: E_p polarized in the plane of incidence; and E_s polarized normal to the plane of incidence. Spectral resolution was 0.2 cm⁻¹ full width at half-maximum (FWHM), and frequency accuracy was within ± 0.05 cm⁻¹. Further details about the apparatus and procedures are found in Ref. 1.

The spectra in Fig. 1 were recorded at an equilibrium pressure of 6.9×10^{-8} mbar of CO₂, with the substrate at 86.2 K. Bulk CO₂ does not condense under these conditions. Two signals were observed near the band origin of the molecular asymmetric stretch (ν_3 , 2349 cm⁻¹). The peak frequencies were 2349.0 and 2340.1 cm⁻¹, independent of polarization. The absolute intensity of these signals was independent of time. Furthermore, when the equilibrium pressure was increased by an order of magnitude the intensity of these signals did not change. The spectra represent a saturated monomolecular layer.

Other experiments indicate that only one kind of adsorption site is significantly populated. The system has been observed at equilibrated submonolayer coverages¹ and with vibrationally decoupled isotopomers present.⁶ These data rule out multiple trapping sites as an explanation for the multiple signals. Also, the asymmetric stretching mode of CO₂ is nondegenerate and far removed from the symmetric stretch (ν_1 , 1388 cm⁻¹). The doublet in Fig. 1 is apparently an effect of resonant coupling among molecular ν_3 modes. Such multiple collective resonances occur when an ordered array of coupled oscillators contains more than one oscilla-

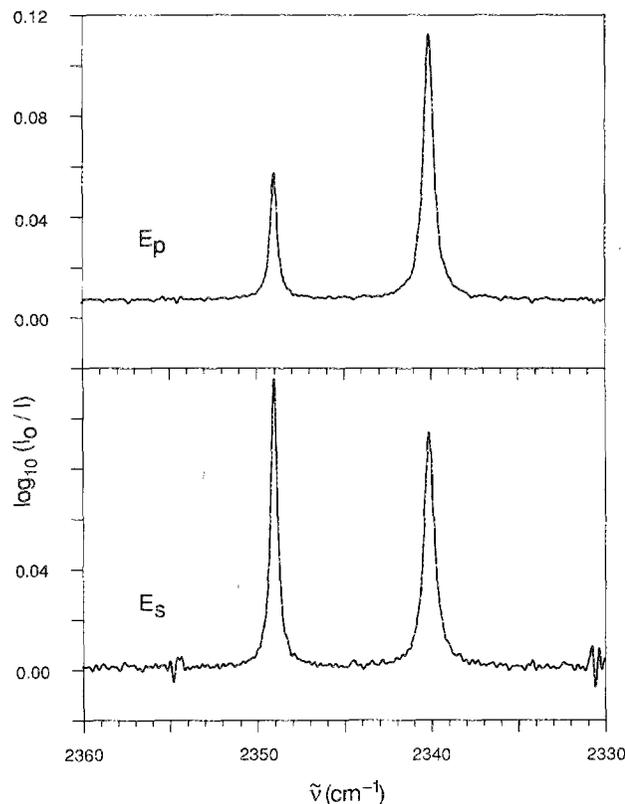


FIG. 1. E_p - and E_s -polarized infrared spectra of a CO_2 monolayer on $\text{NaCl}(100)$. The temperature of the substrate was 86.2 K, and CO_2 pressure was maintained at 6.9×10^{-8} mbar.

tor per unit cell. This effect is known to spectroscopists as correlation field (or "factor group") splitting.¹⁰

III. DISCUSSION

A. Photometry

The oriented gas model ignores all influences on absorbance intensity except geometric ones. Since the E_s and E_p electric fields are orthogonal, the relative intensities of the corresponding absorbance signals can be related to the orientation of molecular transition dipoles in the monolayer. To this end we extend the Beer-Lambert law to include the relative orientations of the probing electric field and the absorbing transition dipole.

The coordinate system is illustrated in Fig. 2. The z axis is normal to the surface. The intersection of the plane of infrared incidence and the plane of the surface is the x axis. The orientation of the molecular transition dipole μ is given by two angles. The degree of tilt from the z axis is α . The angle between the x axis and the projection of μ into the x - y plane is β .

Expressions for integrated absorbance are obtained by resolving both the incident radiation and the integrated molecular cross section into x , y , and z components. For radiation incident on the substrate at Brewster's angle we have derived the following relations²:

$$\tilde{A}_p = \frac{NS}{2.303 \cos \theta} (\bar{\sigma}_z \sin^2 \theta + \bar{\sigma}_x \cos^2 \theta), \quad (1)$$

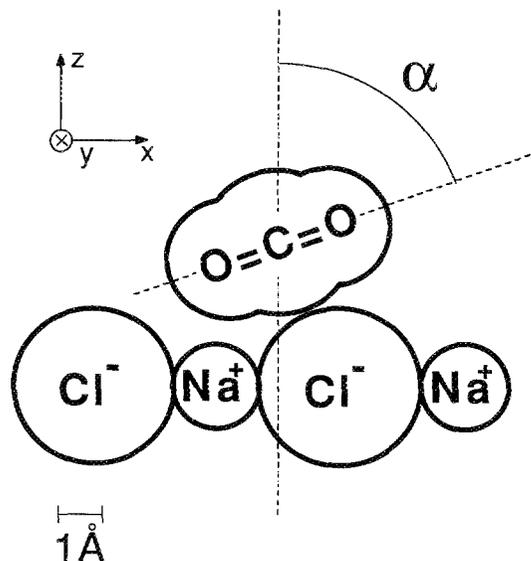


FIG. 2. Oblique adsorption site for CO_2 on $\text{NaCl}(100)$. The van der Waals contour of CO_2 , and the ionic radii of Na^+ and Cl^- are outlined. All pictured nuclei are coplanar. Tilt angle $\alpha = 68^\circ$ was determined from the spectra in Fig. 1. Also shown is the coordinate system used for our photometric calculations.

$$\tilde{A}_s = \frac{2NS}{2.303 \cos \theta (1 + n^2)} (\bar{\sigma}_y), \quad (2)$$

where N is the number of surfaces interrogated, S is the surface density of adsorbates, and $\bar{\sigma}_x$, $\bar{\sigma}_y$, and $\bar{\sigma}_z$ are the components of integrated molecular cross section. The angle of infrared incidence θ is 60° in our experiment. This satisfies the Brewster conditions for total transmittance of E_p radiation, so that the substrate is nonreflecting as well as nonabsorbing. Therefore, the E_p experiment is well suited to oriented gas analysis. E_s radiation, however, is partially reflected by the substrate. This reduces the \tilde{A}_s integrated absorbance by a factor of $2/(1 + n^2)$, where n is the index of refraction of the substrate. Though easily derived, this is an *ad hoc* addition to the oriented gas model.²

It remains to relate the integrated cross section of the gas-phase molecule ($\bar{\sigma}_g$) to the effective integrated cross sections ($\bar{\sigma}_x$, $\bar{\sigma}_y$, $\bar{\sigma}_z$) of an oriented molecule. The empirical $\bar{\sigma}_g$ is an average over all orientations, so that the components of the transition dipole are shared equally among the three Cartesian coordinates. If a molecule is locked *parallel* to the probing electric field, its integrated cross section becomes $3\bar{\sigma}_g$. For a general orientation this is reduced by a function of angles α and β . Projections of the transition dipole along the space-fixed x , y , and z axes couple with the corresponding components of the electric field \mathbf{E} . Evaluation of $|\mu \cdot \mathbf{E}|^2$ produces the trigonometric terms in the equations below:

$$\bar{\sigma}_x = 3\bar{\sigma}_g \sin^2 \alpha \cos^2 \beta, \quad (3)$$

$$\bar{\sigma}_y = 3\bar{\sigma}_g \sin^2 \alpha \sin^2 \beta, \quad (4)$$

$$\bar{\sigma}_z = 3\bar{\sigma}_g \cos^2 \alpha. \quad (5)$$

Subscripts x , y , and z specify the field direction to which each component is sensitive.

The angle β requires special consideration. There are four

equivalent directions on the NaCl (100) surface, but this may not be true of the CO₂ layer. It is possible that the adsorbate forms separate, structurally equivalent rotational domains distinguished only by the value of β . Our experiment probes macroscopic regions of four surfaces; we can be certain that a large number of independent regions are present. Therefore, the spectra represent the average behavior all possible rotational domains. To incorporate this in the photometric model, we average Eqs. (3) and (4) over an even distribution of β . Using $\langle \sin^2 \beta \rangle = \langle \cos^2 \beta \rangle = 1/2$ we obtain

$$\bar{\sigma}_x = (3\bar{\sigma}_g \sin^2 \alpha)/2, \quad (6)$$

$$\bar{\sigma}_y = (3\bar{\sigma}_g \sin^2 \alpha)/2. \quad (7)$$

Since the direction normal to the surface is the same for all rotational domains, the molecular tilt angle (α) is unambiguous.

On substitution of Eqs. (5)–(7) into Eqs. (1) and (2) the ratio of integrated absorbances becomes

$$\frac{\tilde{A}_p}{\tilde{A}_s} = (1 + n^2) \left(\frac{\cos^2 \alpha + \sin^2 \theta + \frac{1}{2} \sin^2 \alpha \cos^2 \theta}{\sin^2 \alpha} \right). \quad (8)$$

Solving for α , with $\theta = 60^\circ$,

$$\alpha = \tan^{-1} \left(\frac{6}{[8(\tilde{A}_p/\tilde{A}_s)/(1 + n^2)] - 1} \right)^{1/2}. \quad (9)$$

To calculate α , the molecular tilt angle, with Eq. (9) we use the ratio of total integrated absorbances $\tilde{A}_p/\tilde{A}_s = 0.81$. For sodium chloride the index of refraction is $n = 1.52$.¹¹ Equation (9) gives $\alpha = 68^\circ$.

With molecular tilt determined, Eqs. (1) and (2) can be used individually to predict integrated absorbances. We use $N = 4$, $\theta = 60^\circ$, $\bar{\sigma}_g = 1.1 \times 10^{-16}$ cm molecule⁻¹.¹² The adsorbate density is chosen to be the same as the density of sodium–chlorine ion pairs at the surface, $S = 6.3 \times 10^{14}$ molecule cm⁻².¹³ This will be justified below. For the E_p experiment, the predicted value of \tilde{A}_p is 0.15 cm⁻¹, while 0.13 cm⁻¹ was observed. For E_s the predicted area is $\tilde{A}_s = 0.18$ cm⁻¹, while 0.16 cm⁻¹ was observed.

Equation (9) was derived for the total integrated absorbance of each polarization. Since the doublet is a correlation field effect, the equation can be applied separately to each collective mode. The band area ratio (\tilde{A}_p/\tilde{A}_s) for the higher-frequency signal is 0.45, which suggests a tilt angle for this transition dipole of $\alpha_h = 84^\circ$. The ratio is 1.1 for the lower-frequency resonance, which corresponds to a transition dipole tilt of $\alpha_l = 62^\circ$. These angles will be used later to assign the symmetry of the doublet components.

B. Symmetry

The CO₂/NaCl(100) system has been the subject of several calculations.^{7–9} Various minima of the one-molecule adsorption potential have been located. Only one of these has an oblique molecular axis. It is illustrated in Fig. 2. When the tilt angle is 45°, the energy of interaction between the quadrupole field of one CO₂ molecule and the ionic charges of NaCl(100) is minimized.

Our data show that the CO₂ molecules are tilted. We con-

clude that they are adsorbed at the recognized oblique sites, but with the observed tilt angle $\alpha = 68^\circ$. It remains to construct a lattice of such adsorbates which is consistent with the data when correlation field coupling is invoked.

Our discussion of intermolecular geometry begins with two sound assumptions. First, it is assumed that the CO₂ molecules are packed at a density of one per exposed sodium–chlorine pair, or 6.3×10^{14} molecule cm⁻². This is only 6% lower than the density of a (100) plane of solid CO₂.¹⁴ Theoretical models are very sensitive to this parameter; their success (described below) supports the chosen value.

Second, since the absorbed infrared wavelengths are four orders of magnitude larger than the dimensions of a carbon dioxide molecule we are justified in the approximation that the radiation field is spatially invariant. A spatially invariant field can only excite vibrations which have a wave vector equal to zero. This can be stated as a selection rule: In order to be infrared active, a collective vibrational mode must be totally symmetric with respect to translation. In other words, all unit cells must vibrate in phase.^{10,15}

Our data specify only the molecular tilt angle. Intermolecular forces in a saturated monolayer are certain to distort the oblique adsorption site, which was derived for the zero-coverage limit. The precise molecule-to-surface geometry is not known. Therefore, in the following discussion the symmetry-breaking properties of the substrate are suppressed. The adsorbed layer is considered in isolation, as a two-dimensional crystal of CO₂ molecules. This physical picture is coherent with the oriented gas approach taken thus far.

If a structure is periodic in three dimensions, its symmetry is described by one of 230 space groups.¹⁶ Because an ordered monolayer has only two degrees of translational symmetry its analysis is restricted to 80 plane groups.¹⁷ These describe the 80 unique patterns which can be produced by repeating a three-dimensional unit cell on the points of a two-dimensional lattice. Plane groups include nonsymmorphic elements: screw axes (C^s) and glide planes (σ^g). This treatment is appropriate for the general case of a monomolecular layer since all nuclei are not necessarily coplanar. The plane groups are to be distinguished from the 17 two-dimensional space groups of crystallography, which are strictly planar.¹⁶

The discussion in preceding sections can be used to identify constraints on the symmetry of the CO₂ layer. First, consider the possibility of rotational axes perpendicular to the layer. Since the molecules are tilted, their collective in-phase ν_3 vibration must be infrared active. If any C_2 exists, the transition dipole for this mode must also be perpendicular to the layer. However, both active modes were observed in the E_s -polarized experiment. Each must have a component of its transition dipole parallel to the layer. Therefore the layer has no C_2 (or C_3 , C_4 , C_6) axes. This eliminates 54 of the 80 plane groups from consideration.

Second, we apply the assumption that the wave vector is exactly zero for the observed vibrations. The active modes are totally symmetric with respect to translation. This allows pure translational operations to be factored out of the plane groups, leaving “factor groups” which are strictly isomorphic to point groups. Therefore, the active vibrational modes

are described by point group character tables. The 26 remaining plane groups represent six factor groups: C_1 , C_2 , C_i , C_s , C_{2h} , and C_{2v} . Further eliminations are made by considering the character tables appropriate for these groups. The observed unit cell contains at least two symmetry-related molecules, which produce two nondegenerate infrared active vibrational modes. Factor groups C_1 and C_i are insufficient. Also, one of the observed transition dipoles is oblique with respect to the layer; it interacts with at least two components of the electric field vector (including μ_z). Therefore, factor group C_{2v} is impossible. We are left with 14 plane groups, which reduce to factor groups C_2 , C_s , C_{2h} .

Finally, prospective structures are considered. There is no upper limit to the number of molecules per unit cell. In order to find the simplest model which is consistent with our data, we first evaluate structures with the lowest possible number, 2. Having assumed an adsorbate density of one molecule per surface unit cell, and using the adsorption site from Fig. 2, six different structures are possible. Three of these have C_z axes, thus may be eliminated from consideration. In two of the remaining three structures, individual Na or Cl ions are shared by two adsorbed molecules. Given the van der Waals radius of CO_2 (as shown in Fig. 2) this is sterically unreasonable. Thus one most likely structure remains.

An extended portion of the proposed geometry is illustrated in Fig. 3, where the monolayer has been displaced from the surface along z . The layer exhibits four symmetry operations: identity (E), inversion (i), screw rotation (C_2^s), and glide reflection (σ^s). These form a primitive rectangular plane group which is analogous to the C_{2h} point group. The unit cell contains two molecules; therefore, it has two collective ν_3 modes. The out-of-phase combination is in symmetry representation A_u . It is infrared active, with a transition dipole parallel to the layer. The in-phase combination is in symmetry class B_u . It is infrared active with an oblique transition dipole. On geometric grounds the collective in-phase dipole is expected to be tilted 60° from the layer normal. We may now use the results from the photometry section to assign the symmetry representations to the observed reson-

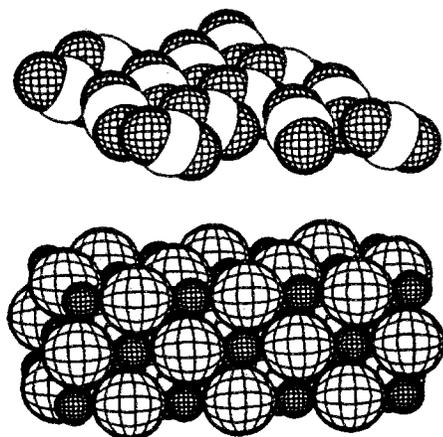


FIG. 3. Proposed structure of CO_2 on $\text{NaCl}(100)$. The adsorbed layer (upper portion) has been displaced from the substrate (lower portion) along the surface normal. Each CO_2 molecule occupies an identical oblique site (Fig. 2); a primitive unit cell of the layer contains two molecules.

ances. The high-frequency vibration, 2349.0 cm^{-1} , was determined to have its transition dipole tilted to $\alpha_h = 84^\circ$. We assign this resonance to the A_u -symmetric collective mode (expected tilt of 90°). The low-frequency component, 2340.1 cm^{-1} , is assigned to the B_u mode. The observed tilt of this transition dipole, $\alpha_l = 62^\circ$, is close to the geometric value of 60° .

C. Simulations

Photometry and symmetry considerations are sufficient to suggest a monolayer structure. A stringent test of our explanation is to model the proposed structure formally and predict its infrared spectrum. Two such efforts are summarized below.

Chen and Schaich use an extension of classical Fresnel optics to model the behavior of adsorbed layers.¹⁸ They have simulated the $\text{CO}_2/\text{NaCl}(100)$ system proposed in Fig. 3.¹⁹ The overlayer was modeled in microscopic detail, while the substrate was considered as a homogeneous and nonpolarizable dielectric medium. Chen and Schaich were able to reproduce the observed spectra by adjusting several parameters. Significantly, the vibrational polarizability (hence infrared cross section) was reduced by 19% from the gas phase value. This correction is typical of electronic changes which occur in condensed phases. It indicates the extent to which this system deviates from oriented gas behavior.

Dissekkamp and Ewing have modeled the CO_2 layer by using the linear variation method of approximate quantum-mechanical calculation.²⁰ A finite two-dimensional cluster was described with basis functions composed of molecular harmonic oscillators in $v = 0$ and $v = 1$ states. The Hamiltonian operator contained only one coupling term: pairwise transition dipole interaction of molecular ν_3 oscillators. The calculation was performed on a cluster of 400 CO_2 molecules ordered as in the upper portion of Fig. 3. The molecules were assumed to retain their gas-phase properties, but the molecular tilt was reduced to 61° . This model clearly maintains the oriented gas perspective. The resulting spectrum is in striking agreement with our observations. The doublet is reproduced, and the calculated splitting energy (11.0 cm^{-1}) is slightly greater than observed (8.9 cm^{-1}). Such close prediction of a subtle coupling effect corroborates the proposed monolayer structure and vibrational analysis.

D. Overview

We have shown how the oriented gas model of physisorption is used for the analysis of monolayer structure. It allows the photometry and symmetry of an adsorbed phase to be formalized. In addition, it can be the basis of effective quantum-mechanical simulation of such systems. This physical approximation is clearly justified for CO_2 on $\text{NaCl}(100)$. For this case it is valid to consider the surface as an essentially passive template, and the adsorbate as a two-dimensional molecular crystal. Indeed, the layer structure we have proposed is a slightly distorted analog of the (100) plane of molecules in solid CO_2 .

The oriented gas model is certain to break down for some adsorbates and classes of investigation. The CO_2 study in-

voled a nondegenerate internal vibration with a relatively large transition dipole. External and degenerate modes will be sensitive to asymmetry of the adsorption site, and weak oscillators will reveal electronic perturbations by the substrate. We are experimenting with other adsorbates (acetylene, methane, formaldehyde) which will test the utility and limits of this conceptual tool.

ACKNOWLEDGMENTS

The authors thank Dr. Kirsten Streib for producing Fig. 3. This work was financed by the National Science Foundation.

^{a)} To whom correspondence may be addressed.

¹ O. Berg and G. E. Ewing, *Surf. Sci.* **220**, 207 (1989).

² H. H. Richardson, H.-C. Chang, C. Noda, and G. E. Ewing, *Surf. Sci.* **216**, 93 (1989).

³ Y. Kozirovski and M. Folman, *Trans. Faraday Soc.* **62**, 1431 (1966).

⁴ J. Heidberg, R. D. Singh, and H. Stein, *Ber. Bunsenges. Phys. Chem.* **82**,

54 (1978).

⁵ J. Heidberg and D. Hoge, *Surf. Sci.* **189/190**, 448 (1987).

⁶ J. Heidberg *et al.*, *Vacuum* **38**, 275 (1988).

⁷ T. Hayakawa, *Bull. Chem. Soc. Jpn.* **30**, 124, 236, 243, 332 (1957).

⁸ J. Heidberg, R. D. Singh, and C. F. Chen, *Z. Phys. Chem. (NF)* **110**, 135 (1978).

⁹ B. Deprick and A. Juig, *Chem. Phys. Lett.* **110**, 150 (1984).

¹⁰ P. M. A. Sherwood, *Vibrational Spectroscopy of Solids* (Cambridge University London, 1972).

¹¹ *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, Orlando, FL, 1985).

¹² S. S. Penner, *Quantitative Molecular Spectroscopy and Gas Emissivities* (Addison-Wesley, Reading, MA, 1959).

¹³ R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963), Vol. 1.

¹⁴ A. D. Buckingham, *Quart. Rev.* **13**, 183 (1959).

¹⁵ R. Zbinden, *Infrared Spectroscopy of High Polymers* (Academic, New York, 1964).

¹⁶ N. F. M. Henry and K. Lonsdale, Eds., *International Tables for X-ray Crystallography* (Kynoch, Birmingham, England, 1952), Vol. 1.

¹⁷ S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (Academic, New York, 1969).

¹⁸ W. L. Schaich and W. Chen, *Phys. Rev. B* **39**, 10714 (1989).

¹⁹ W. Chen and W. L. Schaich, *Surf. Sci.* **220** (1989) L733.

²⁰ R. S. Disselkamp and G. E. Ewing, *J. Chem. Soc. Faraday Trans.* (in press).