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Vibrational Spectroscopy and Two-Dimensional Structure of Molecular Layers on NaCl(100)

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Abstract

We have measured polarized infrared transmission spectra of a variety of molecules physisorbed to NaCl(100). Here we discuss the relation between vibrational spectroscopy of an adsorbate and the geometrical structure of a monomolecular layer. Spectra and proposed structures of CO, CO_2, C_2H_2 and CH_4 layers on NaCl(100) are presented as examples.

1. INTRODUCTION

Molecular physisorption offers unique opportunities for the study of weakly interacting chemical systems. A surface can impose order among adsorbates, open relaxation channels, and modify photochemical processes. Although these effects are difficult to observe, the nature of a monomolecular layer simplifies their analysis. There is considerable scientific utility in a well-defined, reduced-dimensional, heavily-hyphenated phase of this kind.

The spectroscopic study of adsorption to sodium chloride began with DeBoer's work on color centers [1]. Much later Kozirovsky and Folman employed alkali halides as substrates to record infrared spectra of physisorbed molecules [2]. The crystal was sublimed onto a cold window under vacuum, forming a highly divided, clean, transparent film. Similar techniques were developed in other laboratories and are still in use [3-5]. For certain applications, however, the utility of films is limited by the random orientation and structural heterogeneity of the adsorption sites. These difficulties have been overcome recently through the use of single crystals as substrates [6,7]. Vibrational spectra of unprecedented sensitivity and resolution have been recorded.

In our laboratory we prepare layers of molecules on the

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(100) cleavage plane of a large sodium chloride crystal. We then record infrared spectra of the layers' vibrational resonances. A common element of our adsorption studies is the question of monolayer structure. This paper will discuss the application of vibrational spectroscopy to structural problems. Our perception of these systems is grounded in two aspects of the experiment: first, that the adsorbed layer is formed in equilibrium with the gas; second, that the observed resonances originate as internal modes of isolated adsorbate molecules. Our analysis traces the modification of these modes by a variety of mechanisms, all of which are sensitive to structural properties of the layer. Four adsorbates--carbon monoxide, carbon dioxide, methane, and acetylene--illustrate the range of physical effects involved. Furthermore, they demonstrate how the experimental conditions cited above limit the scope of our investigation.

2. PROCEDURES AND RESULTS

The following description of procedures is general to the four adsorbates under discussion. It covers only those instrumental constraints which justify our subsequent analysis. Specific conditions for each adsorbate are found in other publications [8-11].

The NaCl substrate is prepared by cleaving a single-crystal boule along (100) planes. Two slabs are mounted within an ultrahigh vacuum chamber. The beam from a commercial Fourier transform infrared spectrophotometer passes through the chamber and both crystals; its angle of incidence is 60° for each surface. A polarizer further restricts the infrared beam to an E_s or E_p configuration. The electric field vector of E_s light is parallel to the surface in a [100] direction. E_p light has components both parallel (along [100]) and perpendicular to the surface.

Atmospheric adsorbates are removed from the crystals by heating to 100°C under vacuum. Then the crystals are cooled, and a pressure of the desired adsorbate is maintained by steady-state leaking and pumping. Spectra are recorded after the gaseous and adsorbed phases reach equilibrium. The accessible pressure range is 10^{-9} to 10^{-5} mbar. This limits the range of useful dosing temperatures; the surface must be cold enough to develop an observable coverage of adsorbates, yet above the bulk condensation point. Characteristic temperatures for the experiments reviewed below are 40-100 K. The remaining thermodynamic degree of freedom for adsorbed phases--coverage--is controlled by adjustment of temperature and pressure. All of the spectra presented below were recorded under conditions known to produce a saturated monomolecular layer.

At 55 K, under 1×10^{-5} mbar of carbon monoxide (CO), a single infrared absorption is observed with E_p-polarized light. It is centered at 2155.09 cm^{-1} (+13 cm^{-1} from the gas-phase origin) and is 0.42 cm^{-1} wide (FWHM). No absorbance is observed with E_s light [8]. Frequent repetition of this experiment, and experience with a variety of NaCl samples, adsorbates, and contaminants, allow us to use CO spectroscopy as a sensitive diagnostic probe of the surface. We are confident that the substrate for the experiments described here is clean NaCl(100).

At 86.2 K, under 6.9×10^{-8} mbar of carbon dioxide (CO_2), two signals are observed near the gas-phase origin of the asymmetric stretch (ν_3). Figure 1 shows that they are present in the E_s spectrum as well as E_p, but with different relative absorbance intensities. We have also observed equilibrated submonolayers [10]. Both the extent of splitting and the relative intensities of the doublet members are independent of fractional coverage (θ) in the range $\theta = 0.3$ to $\theta = 1.0$. Heidberg and co-workers have recently reported similar spectra for this system [12]. In addition, they have observed four bands near the origin of the doubly degenerate bending mode.

At 77.7 K, under 5×10^{-8} mbar of acetylene (C_2H_2), three signals are observed near the gas-phase origin of the asymmetric C-H stretch (ν_3). The E_s and E_p spectra are qualitatively alike: relative areas among the bands are insensitive to polarization, but the absolute area of the E_s multiplet is greater than that of E_p. Dynamic splitting mechanisms can be separated from static ones by the observation of vibrationally decoupled isotopomers. To this end, figure 2 compares the spectrum of a neat C_2D_2 monolayer to the spectrum of a 15% C_2D_2 minority in an 85% C_2H_2 monolayer. The decoupled sample has only two resonances in this frequency region.

Figure 3 shows the E_p spectrum of adsorbed methane (CH_4) at 42 K, under 5×10^{-8} mbar. One absorbance is observed near the origin of the infrared active C-H stretch (ν_3), while two bands are found near the active C-H bend (ν_4). Both of these modes are triply degenerate for a gas-phase molecule. The principal difference in an E_s spectrum is the absence of the 1320 cm^{-1}

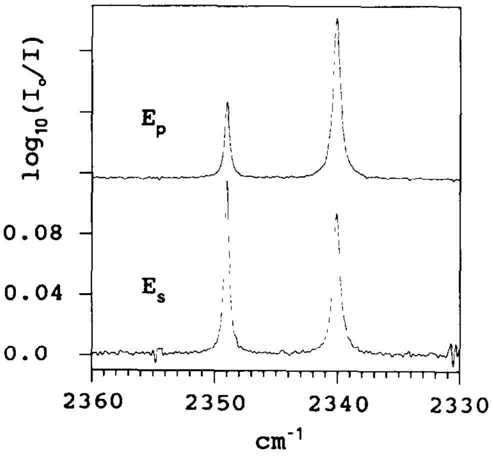

Fig. 1. CO_2 on NaCl(100)

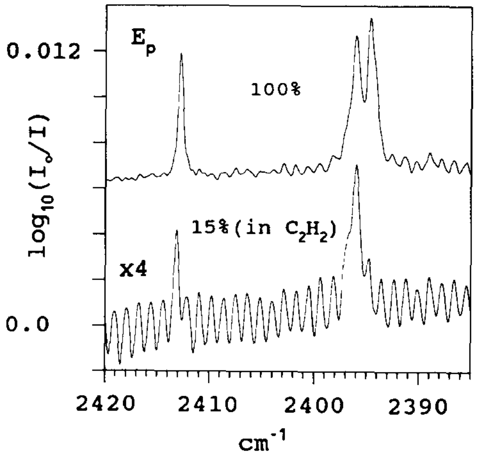

Fig. 2. C_2D_2 on NaCl(100)

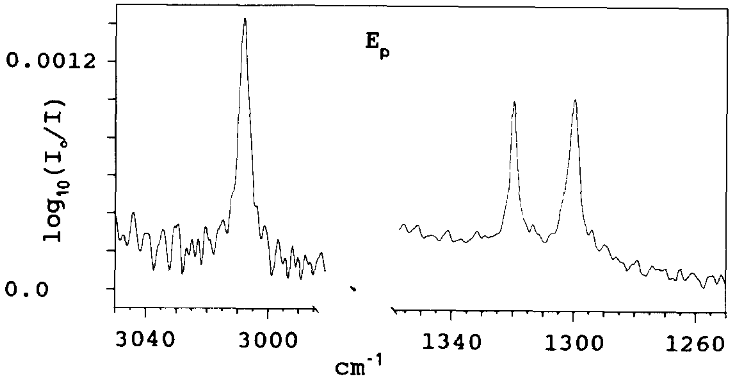

Fig. 3. CH_4 on NaCl(100)

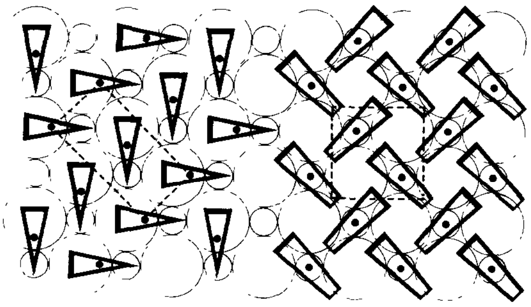

Fig. 4. Monolayer structures for CO_2 (left) and C_2H_2 (right)

resonance.

3. DISCUSSION

Following are the structural models that we propose:

CO: The bond axis is perpendicular to the surface. A saturated monolayer contains 6.3 x 10^{14} molecules cm^{-2}--this is the density of Na^+Cl^- ion pairs at the surface. Submonolayers occupy a random distribution of available sites.

CO_2: The bond axis is tilted 68° from the surface normal. Submonolayers are condensed into two-dimensional islands. A saturated monolayer contains 6.3 x 10^{14} molecules cm^{-2}, and the layer unit cell contains two equivalent molecules. The structure is shown schematically in figure 4 (left side): circles represent surface ions, triangles represent CO_2 molecules tilted out of the plane of the illustration. A primitive unit cell of the layer is outlined.

C_2H_2: The saturated monolayer contains two sublattices of molecules tilted 82° from the surface normal. One set contains two equivalent molecules per unit cell (figure 4, right side); the other set forms half of a second layer.

CH_4: Individual molecules have two hydrogen atoms directed toward the surface, two directed away. The surface density and layer unit cell are not known.

We use three kinds of arguments to extract structural information from infrared spectra: thermodynamics, photometry, and symmetry. Each of these is discussed below, with the four adsorbates used as examples.

3.1 Thermodynamics

Because our spectra are collected at equilibrium, each temperature/pressure/coverage datum is a point on a phase diagram. We map this thermodynamic surface in the form of adsorption isotherms. These characterize the phase properties of a molecular layer.

The shape of an adsorption isotherm is related to the importance of adsorbate-adsorbate interactions in comparison to adsorbate-substrate bonds. This in turn governs how adsorbates will be distributed among available sites. One extreme is the Langmuir model, which assumes that adsorption sites are localized and independent [13]. This model is insensitive to the spatial arrangement of occupied sites; in other words, adsorbates which display Langmuir-type isotherms are randomly distributed. Carbon monoxide adsorbed to NaCl films [4] and single crystals [14] follows the Langmuir model. Therefore this phase is pictured as a two-dimensional gas.

If adsorbates are mobile or mutually attracting they deviate from the Langmuir approximation. Discontinuity in the slope of an isotherm is characteristic of a two-dimensional phase transition. Both CO_2 and C_2H_2 show such steps [7,10]. We expect islands of a dense phase to be present, perhaps with translational order. This is confirmed by the observation of correlation field splitting in submonolayers. Isotherm models that incorporate lateral interaction have been developed. The quasi-chemical approximation assumes that these attractions act independently between nearest-neighbor pairs [13]. When fit to empirical C_2H_2/NaCl(100) isotherms, the model suggests a total nearest-neighbor interaction of 4 kJ mole^{-1}.

Another thermodynamic clue about monolayer structure is provided by theoretical models of the molecule/surface adsorption potential. A model can narrow the range of plausible geometries to the point that only one is consistent with spectroscopic observations. We have benefited from the work of Gevirzman et al. [15] and Gready et al. [16] (CO); Heidberg et al. [17] and Stone [18] (CO_2); and Singh et al. [19] (CH_4).

3.2 Photometry

There is reason to be hopeful that the photometry of our single-crystal physisorption experiment can be quantified. The absolute orientations of the substrate and probing radiation are known, and the beam is incident on the substrate at a Brewster's angle. Furthermore, the interactions that cause adsorption to a dielectric substrate are weak. Electrostatic and dispersion forces do not seriously perturb the internal vibrational resonances that we observe. Therefore it is reasonable to begin our analysis using the electronic parameters of isolated adsorbate species. Finally, since the substrate does not contain free electrons we need not consider any modification of molecular selection rules due to image dipoles. Taken together, these simplifications constitute the "oriented gas" model. It ignores all influences on the photometric behaviour of our sample except its non-random orientation.

Consider first the variation of integrated absorbance with infrared polarization. It is obvious that a transition dipole oriented perpendicular to the surface will not absorb E_s-polarized light, since this light has no perpendicular component. This is the ground of our empirical CO monolayer structure [6]. Similarly, a missing band in the E_s spectrum of CH_4 informs us that the transition dipole of one bend is normal to the surface [11]. Transition dipoles which are *parallel* to the surface and produce structured spectra (through correlation field splitting, for example) follow a less obvious rule: Since the absorbed components of electric field differ only in absolute magnitude, the E_s and E_p spectra must differ only by an overall scale factor. Thus, for adsorbed acetylene the qualitative similarity of E_s and E_p spectra indicates immediately that the molecules are almost parallel to the surface. The oriented gas model provides a formal relation between transition dipole tilt and the variation of absorbance signal with polarization. We can develop the Beer-Lambert law in surface-fixed coordinates, and average *only* over the rotational domain angle. Solving for tilt angle α (measured from the surface normal)

$$\alpha = \tan^{-1}\left[\frac{\sin^2\theta}{\dfrac{\bar{A}_p/\bar{A}_s}{1+n^2} + \dfrac{\cos^2\theta}{2}}\right], \qquad (1)$$

where $\bar{A}_p/\bar{A}_s$ is the ratio of E_p to E_s integrated absorbances, θ is the angle of infrared incidence, and n is the substrate's index of refraction [9]. This expression assumes that n and θ satisfy the Brewster condition for complete transmission of E_p light [8]. With $\theta = 60°$ and $n = 1.52$, equation (1) gives $\alpha = 68°$ for CO_2, and $\alpha = 82°$ for C_2H_2.

The oriented gas model can also relate monolayer structure to absolute absorbance band areas. Under the same assumptions as equation (1) we find

$$\bar{A}_p = \frac{3\ NS\ \tilde{\sigma}_g \left[\cos^2\alpha\ \sin^2\theta + \dfrac{\sin^2\alpha\ \cos^2\theta}{2}\right]}{2.303\ \cos\theta} \qquad (2)$$

$$\tilde{A}_s = \frac{3\ NS\ \tilde{\sigma}_g \sin^2\alpha}{2.303 \cos\theta\ (1+n^2)} \quad , \qquad (3)$$

where N is the number of surfaces probed, S is the two-dimensional density of adsorbates, and $\tilde{\sigma}_g$ is the gas-phase integrated molecular cross section. Three adsorbates illustrate the utility of these equations. First, the photometry of CO_2 is dominated by geometric effects on its large infrared cross section. The oriented gas model converges on a monolayer structure (figure 4) which satisfies equations (2) and (3). Predicted band areas are ~15% larger than observed. This is a surprising success, which lends credence to the underlying assumptions.

For CO, the tilt angle and surface density are known independently of equations (1-3) [6,15,16]. Equation (2) predicts a band area 160% greater than observed. Clearly the cross section of an isolated molecule is not appropriate; in other words, the oriented gas model is invalid. More detailed treatment of this system indicates that polarizability of the layer and chemical perturbation of the C-O bond are both significant [8,20]. The photometry of CO is in general more sensitive to perturbations by the substrate than that of CO_2 because the latter molecule has a much larger infrared cross section [21].

For C_2H_2, the oriented gas model again fails to yield a consistent structure. Neither the surface density nor the effective infrared cross section are known on independent grounds. Fortunately equation (1) is independent of these parameters, so that the empirical tilt angle is secure. The structure in figure 4 is supported by general chemical arguments and symmetry considerations. Given this geometry, equations (2) and (3) suggest an empirical infrared cross section which is more than twice that of gas-phase C_2H_2 molecules [10]. In solid and diametric acetylene this vibration is also enhanced, probably because of intermolecular hydrogen bonding.

3.3 Symmetry

A striking feature of the spectra in figures 1-3 is the multiplicity of bands. These adsorbates illustrate three mechanisms by which an internal vibrational resonance can be split in an adsorbed phase: site multiplicity, static field splitting, and correlation field splitting. Explanations involving the latter two effects require the use of symmetry theory. The first, however, is straightforward. If a monolayer comprises more than one kind of adsorption site, then the population of each site will give a distinct absorbance signal. Since a minority isotopomer is distributed randomly among occupied sites it will exhibit site effects. Thus the large splitting which is observed for neat _and_ minority C_2D_2 must arise from independent sites (figure 2). Static and correlation field effects can be ruled out because the vibration is degenerate and, in 15% concentration, decoupled from its neighbors. On these grounds it is also clear that the smaller splitting _is_ a correlation field effect, and therefore represents a crystalline sublattice (2396 cm^{-1}) with at least two molecules per unit cell. The other sublattice (2413 cm^{-1}) is either disordered, decoupled, or has a trivial unit cell. It is perhaps a half-filled second layer [10].

Experiments indicate that correlation field splitting alone is responsible for the CO_2 doublet in figure 1 [9,12]. The observed resonances are therefore collective vibrations in an array of coupled molecular oscillators. We wish to describe them with an appropriate group-theoretical formalism. The standard treatment of static and correlation field effects is to correlate a point group, site group, and factor group [22]. Nichols and Hexter have extended the Longuet-Higgins (permutation/inversion) group theory in order to describe non-rigid molecular layers [23]. Our CO_2 and C_2H_2 spectra, however, involve nondegenerate modes and contain no evidence of free rotation. The molecular vibrations are modified by interactions strictly within the layer--specifically, transition dipole-transition dipole coupling. A concise characterization of a the relevant symmetry is given by a "plane group" [25] or "diperiodic space group" [24]. Molecular layers and interfaces have a three-dimensional unit cell, but only two degrees of translational symmetry. The character tables for plane groups are easily constructed; they provide a formal connection between monolayer structure and the activity, degeneracy, and polarization of collective vibrational modes. When used with equation (1) this is a powerful tool for the evaluation of proposed structures. It allows us to assign the combinations in a two-molecule array as in-phase (2340.1 cm^{-1} for CO_2, 2396.0 cm^{-1} for C_2D_2) or out-of-phase (2349.0 for CO_2, 2394.6 cm^{-1} for C_2D_2).

The bending mode of gas-phase CH_4 is triply degenerate.

Experiments show that this degeneracy is partially lifted by adsorption to a NaCl film or single crystal [11]. Two adsorption geometries, both centered over a sodium ion, are considered feasible: three hydrogen atoms down, forming a C_s complex with the surface; or two hydrogen atoms down, centered above the sodium-sodium diagonal, forming a C_{2v} complex with the surface [19]. For the molecular point group T_d, a correlation table shows that either site is expected to break the degeneracy completely [26]. This is true of any lower-symmetry complex as well, and sites of higher symmetry are not available on NaCl(100). Only if the surface acts as a homogeneous plane does the three-down complex (now C_{3v}) retain a double degeneracy.

Alternatively, it is possible that the bending degeneracy is broken by the layer of adsorbates itself. It is instructive to consider the simplest cases: one molecule per unit cell, arranged as dictated by the availability of three-down or two-down sites on NaCl(100). Since we are now considering the layer in isolation from the surface, plane group symmetry is sufficient. The plane group which describes a three-down array is isomorphic to point group C_s. Again, all modes are nondegenerate. The plane group which describes a two-down array is isomorphic to point group D_{2d}. Here the degeneracy is not completely broken: we expect a degenerate pair of modes polarized parallel to the layer, and a lone mode polarized perpendicular to the layer. This is consistent with our spectra. More complicated two-down unit cells can also behave in this way; three-down unit cells can not. We find this mechanisms of partial degeneracy-lifting physically more reasonable, and therefore propose a two-down adsorption site for CH_4 on NaCl(100). The extant data are not conclusive. Indeed, the absence of splitting in the stretching mode (also triply degenerate) is a puzzle.

4. SUMMARY

Infrared spectroscopy is a rich source of information regarding the structure of monolayers. For molecular adsorption to an insulator, this technique is by nature sensitive to the density, local symmetry, and absolute orientation of adsorbates. Adsorption isotherms and polarized spectra obtained from a well-defined substrate can be sufficient to determine monolayer structure. The analysis which we have outlined here will at least yield geometric constraints that limit the range possibilities. Our examples suggest that the method is relatively insensitive to microscopic features of the substrate and long-range order in the layer. Complementary experimental methods could provide this information.

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