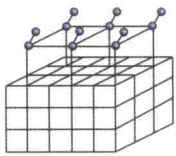
World Scientific Lecture and Course Notes in Chemistry – Vol. 7

Spectroscopy and Dynamics of Orientationally Structured Adsorbates



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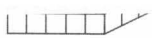

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Spectroscopy and Dynamics of Orientationally Structured Adsorbates

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V. M. Rozenbaum & S. H. Lin

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Preface

The book covers a variety of questions related to orientational mobility of polar and nonpolar molecules in condensed phases, including orientational states and phase transitions in low-dimensional lattice systems and the theory of molecular vibrations interacting both with each other and with a solid-state heat bath. Special attention is given to simple models which permit analytical solutions and provide a qualitative insight into physical phenomena.

A detailed and rigorous treatment offered by the book is intended mostly for specialists and graduate students in solid state theory and surface physics. It may likewise be attractive for scientists studying the properties of impurity subsystems incorporated in a solid-state bulk or adsorbed on a solid surface, as for instance, intercalated compounds. The researchers in academic institutions or industry who are not strictly surface-oriented but are interested in the subjects mentioned can also take advantage of the material, as a special emphasis on methodological essentials and mathematical tools is provided, thus saving a reader from seeking them elsewhere in the literature. On the other hand, to make the book readable also for neophytes in surface science, the authors tried to keep possibly lucid presentation form throughout the main material (with specific mathematical facets put away into appendices) and to offer a wealth of references on orientational surface structures and vibrational excitations in them. The book is supported by two indices; besides an alphabetical listing of subjects and authors, cross-references will enable a reader to easily access the information both on principal concepts involved and on specific adsorbate compositions.

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Chapter 1

Introduction

In the last decade studies on adsorbed molecules and the monolayers formed by them have been receiving a great deal of interest due to diverse features both of applied and fundamental theoretical significance. On the one hand, adsorption and catalysis are extensively used in microelectronics, semiconductor engineering, chemical industry, and biotechnology, which calls for a deeper insight into adsorbate states. On the other hand, a system of adsorbed molecules offers a manifold of facets to be studied: it can be regarded both as an impurity subsystem with respect to a corresponding solid surface and as a quasi-two-dimensional entity in its own right, with all the particular cooperative properties arising from low dimensionality. It is also noteworthy that in most cases an adsorbed molecule is tightly bound to a surface through a single atom, whereas the other atoms (further from the surface) retain considerable mobility. Symmetric arrangement of substrate atoms often admits of several equivalent positions for the atoms of adsorbed molecules, i.e. several equivalent molecular orientations. As a result, the systems concerned are distinguished by high reorientational activity. Provided that intermolecular lateral interactions forming a molecular ensemble are strong enough to remove the orientational state degeneracy for isolated adsorbed molecules, they give rise to orientational ordering. It is evident that changes in temperature may cause phase transitions between orientationally ordered and disordered phases in such systems.

When the concentration of adsorbed molecules is sufficient to form a monolayer, intermolecular lateral interactions become predominating in its orientational structurization and radically change the corresponding spectrum of vibrational excitations, the main source of structural and physicochemical information of the adsorbate. To date a wealth of experimental evidence on adsorbed monolayer structures, relevant monitoring methods, and theoretical approaches has been accumulated and generalized in a number of surveys (see the reference list at the end of Introduction). In view of various factors governing the states of adsorbates, adsorbed monolayers are described, as a rule, on a particular basis, i.e., focusing on a concrete adsorbate/surface combination. Present-day computer-oriented strategies are also adapted to modeling specific systems, with the numerical values of geometrical parameters and interaction constants given. Thus, thorough structural and spectroscopic determinations of concrete character are

mainly performed for adsorbates, which meets the current demands of applied science of materials.

There also exists an alternative theoretical approach to the problem of interest which goes back to "precomputer epoch" and consists in the elaboration of simple models permitting analytical solutions based on prevailing factors only. Among weaknesses of such approaches is an a priori impossibility of quantitative-precise reproduction for the characteristics measured. Unlike articles on computer simulation in which vast tables of calculated data are provided and computational tools (most often restricted to standard computational methods) are only mentioned, the articles devoted to analytical models abound with mathematical details seemingly of no value for experimentalists and present few, if any, quantitative results that could be correlated to experimentally obtained data. It is apparently for this reason that interest in theoretical approaches of this kind has waned in recent years.

Straightforward analytical models, however, receive particular attention in the present book, as they are of unique significance in the comprehension of physical phenomena and, moreover, provide the very language to describe them. To exemplify, recall the effect caused on the phase transition theory by the exactly soluble two-dimensional Ising model. Nor can one overestimate the role of the quasiparticle concept in the theory of electronic and vibrational excitations in crystals. As new experimental evidence becomes available, a simplistic physical picture gets complicated until a novel organizing concept is created which covers the facts known from the unified standpoint (thus underlying the aesthetic appeal of science).

The question now arises of what simplification is possible in the treatment of orientationally structured adsorbates and what general model can be involved to rationalize, within a single framework, a diversity of their properties. Intermolecular interactions should include Coulomb, dispersion, and repulsive contributions, and the adsorption potential should depend on the substrate constitution and the nature of adsorbed molecules. However difficult it may seem, all these factors can be taken into account if we follow the description pattern put forward in this book. Its fundamentals are briefly sketched below.

Analyzing orientational structures of adsorbates, assume that the molecular centers of mass are rigidly fixed by an adsorption potential to form a two-dimensional lattice, molecular orientations being either unrestricted (in the limit of a weak angular dependence of the adsorption potential) or reduced to several symmetric (equivalent) directions in the absence of lateral interactions. In turn, lateral interactions should be substantially anisotropic.

The first terms of the power series obtained by the multipole expansion of the Coulomb intermolecular potential account for dipole-dipole interactions prevailing in systems of polar molecules. As an adequate approximation for ensembles of

nonpolar molecules with quasinormal or planar orientations of their long molecular axes, we can invoke a generalized form resembling the Hamiltonian of dipole-dipole interactions, with the constant values appropriately renormalized. An additional rationale for such a model follows from the fact that the interactions of dynamic dipole moments of vibrational and electronic transitions represent the basic mechanism for a collectivization of the corresponding excitations. It is therefore expedient to simulate lateral interactions just by a Hamiltonian of a dipole-dipole form, with the interaction constants to be fitted. To account for line shapes in vibrational spectra of adsorbed monolayers, the interaction between the adsorbate and the phonon thermostat of a substrate has also to be involved.

In the present book, we aim at the unified description of ground states and collective excitations in orientationally structured adsorbates based on the theory of two-dimensional dipole systems. Chapter 2 is concerned with the discussion of orientation ordering in the systems of adsorbed molecules. In Section 2.1, we present a concise review on basic experimental evidence to date which demonstrate a variety of structures occurring in two-dimensional molecular lattices on crystalline dielectric substrates and interactions governing this occurrence.

To describe the orientation-dependent part of lateral interactions, we invoke a general angular dependence which is equally relevant to quadrupole, dispersion, and repulsive interactions (all contributing only to distance-dependent coefficients). In the next section (Sec. 2.2), much space is given to the fundamentals of the theory of two-dimensional systems with real (long-range and anisotropic) dipole-dipole interactions. Further (in Sec. 2.3) we demonstrate that the ground states for ensembles of nonpolar molecules with quasinormal or planar orientations can be found by minimization of eigenvalues of the Fourier-transformed short-range dipole-dipole interaction tensor with generalized values of coefficients. This approach affords a straightforward and convenient treatment of the ground states and orientational phase transitions for a system of nonpolar molecules (Secs. 2.4 and 2.5).

Chapter 3 is devoted to dipole dispersion laws for collective excitations on various planar lattices. For several orientationally inequivalent molecules in the unit cell of a two-dimensional lattice, a corresponding number of colective excitation bands arise and hence Davydov-split spectral lines are observed. Constructing the theory for these phenomena, we exemplify it by simple chain-like orientational structures on planar lattices and by the system CO_2/NaCl(100). The latter is characterized by Davydov-split asymmetric stretching vibrations and two bending modes. An analytical theoretical analysis of vibrational frequencies and integrated absorptions for six spectral lines observed in the spectrum of this system provides an excellent agreement between calculated and measured data.

In the pivotal Chapter 4, temperature dependences of spectral line shifts and widths are analyzed. To treat them, we have to invoke rather complex concepts of

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the theory of many-particle systems. Indeed, temperature dependences of adsorbate spectral lines, with their frequencies strongly exceeding those of atomic vibrations in a substrate, can be accounted for only provided anharmonic coupling with temperature-sensitive low-frequency modes. It is clear that the latter can be represented by low-frequency vibrations of the same adsorbed molecules which should be bound to a thermodynamic reservoir of the substrate and have, in addition, their intrinsic anharmonicity. The problem becomes even more involved at sufficiently high surface concentration of adsorbed molecules, because in this case both high-frequency and low-frequency molecular modes are collectivized due to intermolecular interactions. First we demonstrate that the low-frequency component of the Hamiltonian referring to excitations in the adsorbate and the substrate can be diagonalized in the wave vector of adsorbate excitations which become resonant (i.e. having finite lifetimes) as a result of harmonic coupling with excitations in the substrate (Sec. 4.1). Then, in the framework of the known exchange dephasing model, we introduce a high-frequency mode with biquadratic anharmonic coupling and invoke the Green's function method of the Markov approximation to derive an exact expression for the spectral function of the local high-frequency vibration (Sec. 4.2). In the event that the resonant low-frequency mode is itself strongly anharmonic and can be described by a finite number of harmonic sub-barrier states, the perturbation theory for the Pauli equation is applied so as to account for an additional dependence of spectral line shift and width for a local vibration on a number of sub-barrier states (determined by the reorientation energy barrier). This is followed by the generalization of the exchange dephasing model, first, to various types of anharmonic coupling between high-frequency and low-frequency modes, and second, to collectivized excitations of an adsorbate (Sec. 4.3). Much consideration is given to the contribution of dipolar dispersion laws to dephasing of high-frequency collective vibrations and a simple model for collective high-frequency and low-frequency molecular modes is formulated. The results gained are applied to interpret temperature dependences of spectral line shifts and widths for local vibrations which are observed for a diversity of realistic adsorption systems, *viz.* molecular complexes with hydrogen bonds, OH/SiO_2, H/Si(111), H(D)/C(111), and CO/NaCl(100)).

The book thus embraces an extended study on a variety of issues within the theory of orientational ordering and phase transitions in two-dimensional systems as well as the theory of anharmonic vibrations in low-dimensional crystals and dynamic subsystems interacting with a phonon thermostat. For the sake of readability, the main theoretical approaches involved are either presented in separate sections of the corresponding chapters or thoroughly scrutinized in appendices. The latter contain the basic formulae of the theory of local and resonance states for a system of bound harmonic oscillators (Appendix 1), the theory of thermally activated reorientations and tunnel relaxation of orientational

states in a phonon field (Appendix 2), and the temperature Green's function technique in the representation of Matsubara's frequency space (Appendix 3). Thus, practically all the relationships are substantiated in detail mathematically, so that a reader needs not retrieve proofs from other sources. Subject and author indices facilitate a search for a material of interest. To conclude, the book is expected to be helpful as a handbook on the theory of vibrations and reorientations of impurity molecules and groups of atoms and also on the theory of orientational structures and cooperative phenomena in adsorbates.

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Chapter 2

Orientational structures of adsorbates

2.1. Brief survey of experimental data and theoretical approaches

Orientations of long axes of adsorbed molecules are dictated by two factors, *viz.* the angular dependence of the adsorption potential and lateral intermolecular interactions including the screening contribution from a substrate. Strong screening of Coulomb interactions along metal surfaces is likely to result in perpendicular molecular orientations, as for instance in the case of the simplest orientational structures formed by CO molecules on various metal surfaces.[1] Unlike metal substrates, dielectric crystalline adsorbents give rise to a diversity of orientational structures in surface molecular monolayers, as long axes of adsorbed molecules are allowed to deflect from the surface-normal direction and their orientation projections onto the surface plane are completely governed by longitudinal lateral interactions (see surveys [2-4] and references cited therein).

Structures of this kind are normally detected by neutron, low-energy electron, and X-ray diffractions. The systems under study can be exemplified by the monolayers N_2,[5-8] O_2[9] (Figs. 2.1, 2.2), CO_2,[10] C_2N_2,[11] CS_2[12] on a graphite surface (long molecular axes lie in the surface plane) or by the monolayer of CO_2/NaCl(100)[13-19] (molecules are slightly surface-inclined) (Fig. 2.3). Each of these orientational configurations can be treated as a two-sublattice monolayer, with the parameters given in Fig. 2.4 and the corresponding values listed in Table 2.1.

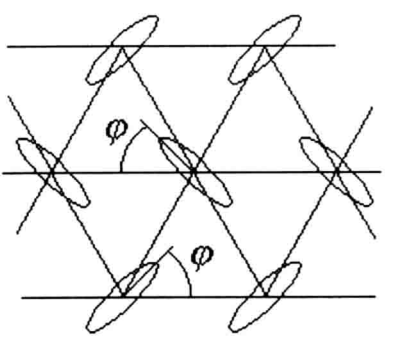

Fig. 2.1. The molecular orientations in the commensurate $\sqrt{3}\times\sqrt{3}$ N_2 monolayer on the graphite basal plane.

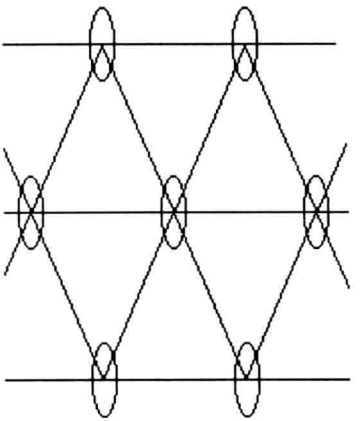

Fig. 2.2. The molecular orientations in the ordered O_2 monolayer on the graphite basal plane.

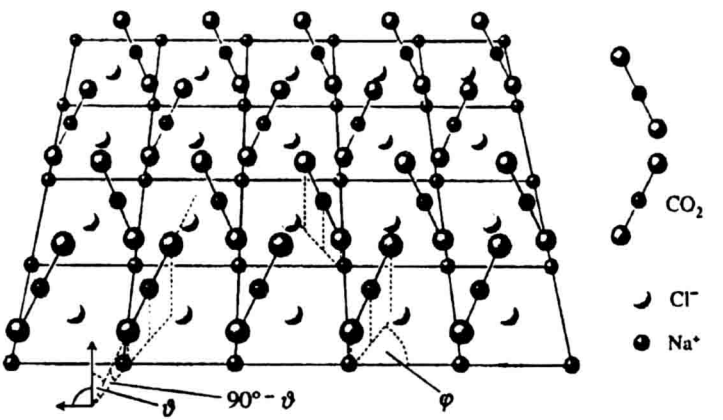

Fig. 2.3. (2x1)-structure of CO_2/NaCl(100) at monolayer coverage.[15-17]

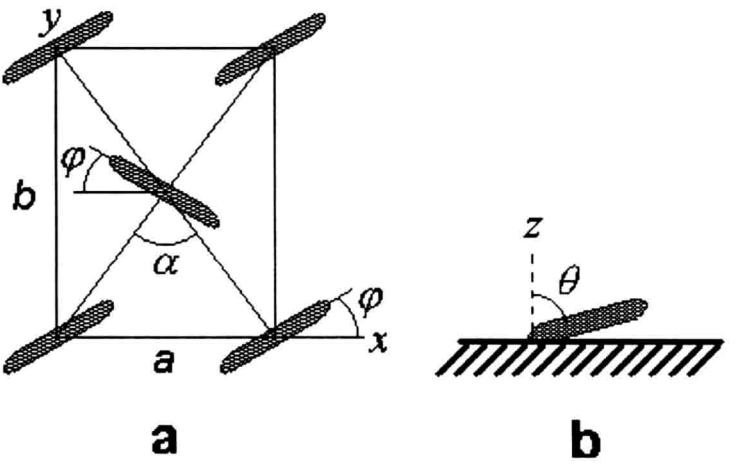

Fig. 2.4. Definition of structural parameters for a two-sublattice monolayer: (a) projections of long molecular axes onto the unit cell; (b) side view showing the tilt of the molecular axis.

Table 2.1. Parameters of orientationally structured adsorbates

Substrate	Molecule	Molecular lattice (Distances in Å)				Orientational structure (Angles in degrees)		Method and Refs.
		S_0	a	b	α	θ	φ	
Graphite	N_2	15.7	4.26	7.38	60	75-90	40-50	[a] [5,6] [b] [7,8]
	O_2	13.5	3.3	8.1	44	90	90	[a] [9]
	CO_2	15.2	4.39	6.93	65	90	41	[c] [10]
	C_2N_2	24.2	6.72	7.22	86	90	35	[b] [11]
	CS_2	24.3	6.02	8.07	73	90	33	[c] [12]
NaCl(100)	CO_2	15.9	3.988	7.976	53	65	49.5	[13-19]

[a] Low-energy electron diffraction (LEED)
[b] Elastic neutron diffraction
[c] X-ray diffraction

Projections of molecular axes onto the surface plane form chain-like structures in which the chains with identically oriented molecules alternate (with the exception of oxygen molecules). The Davydov splitting of spectral lines represents the main spectroscopic manifestation of adsorbed structures with several orientationally inequivalent molecules in the unit cell of a two-dimensional adsorbate lattice. Many

adsorbates, such as CO_2/NaCl(100),[13-17,20-26] CO/NaCl(100),[20,27-32] N_2O/NaCl(100),[33] CO_2,SO_2/CsF(100),[34] HN_3/NaCl(100),[35,36] CO_2/MgO(100),[26,37,38] CO/MgO(100)[38,39] etc. belong to this class. As an example, the monolayer CO_2 on NaCl(100) forms a (2×1) structure with pg symmetry, containing two molecules per adsorbate unit cell (Fig. 2.3). Infrared absorption of CO_2 molecules was observed in the region of the asymmetric stretching vibration ν_3 (~ 2345 cm^{-1}) and the bending mode ν_2 (~ 665 cm^{-1}). The asymmetric stretching vibration appears as a Davydov doublet, the symmetric collective vibrational mode being inclined with respect to the surface, the antisymmetric mode being parallel to the surface (Fig. 2.5).

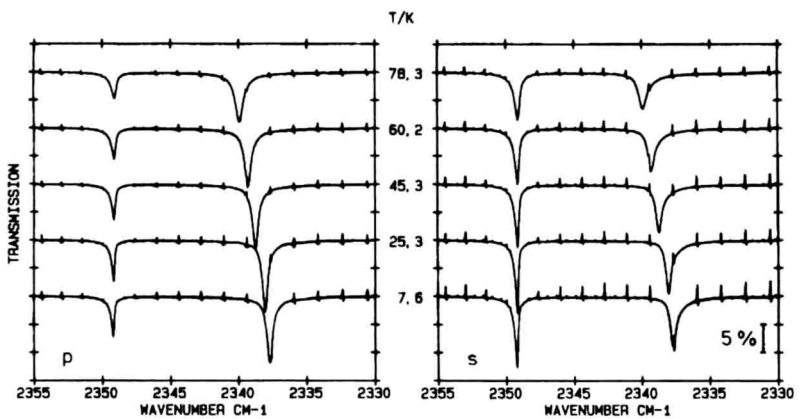

Fig. 2.5. *p*- and *s*-polarized ν_3 transmittance spectra of the monolayer $^{12}C^{16}O_2$/NaCl(100) for different temperatures.[15-17]

The ν_2 bending vibration is a quartet or, in a simplified picture, two Davydov doublets as a consequence of a site-symmetry-induced doublet (see Fig. 2.6).[40] A system of particular interest is CO/NaCl(100): it is characterized by inclined molecular orientations with θ=25^0 and antiferroelectric ordering of chains at low temperatures (see Fig. 2.7) which is removed on the phase transition at $T \approx 25$ K. This structural information is deduced from the observed Davydov splitting of the spectral line for the CO stretching vibrations at 2155 cm^{-1} and T<24 K (see Fig. 2.8).[20,27,28,41-45]

Theoretical treatment of such structures is favored by the fact that the azimuthal component of the angular dependence of the adsorption potential is determined by the arrangement symmetry for the substrate atoms closest to the adsorbate, i.e., by the substrate crystal lattice. As a result, an isolated molecule can have several

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