Vibrational and orientational states of surface atomic groups

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This survey is devoted to the current state of theoretical studies of two-dimensional dipole systems. Systems of hydroxyl groups on the surfaces of oxides have been the most experimentally studied systems. The article examines the orientational states of isolated radicals in local potentials of hindered rotation, various types of orientational ordering of dipoles in two-dimensional lattices, and the appearance of the dipole glass phase in a system with arbitrary filling of lattice sites by particles. Proof is presented of the existence of long-range order in two-dimensional dipole systems, as well as estimates of phase transition temperatures. There is a discussion of the theory of the vibrational spectra of ordered and disordered systems of dipole radicals in various orientational phases. Experimental data are presented on the infrared spectroscopy of surface hydroxyl groups. The data verify theoretical results. Unresolved problems are indicated as well as the prospects for further studies of two-dimensional dipole systems.

1. INTRODUCTION

Ever increasing interest in two-dimensional systems is based on the tempestuous development of studies of solid surfaces and their many applications. Interest has also been stirred by the properties of non-three-dimensional phase transformations. The ability of a surface to adsorb a large number of extrinsic particles leads to the statement of new problems on the behavior of extrinsic two-dimensional subsystems with direct and indirect (through the substrate) interactions between particles.¹ The problem arises of ordering dipole particles on the surface, which is a two-dimensional analog of the same problem of noncentral ions in crystals.²

Hydroxyl groups on the surfaces of oxides have been the most studied two-dimensional dipole systems.³⁻⁸ This is due to their special chemical activity compared to nucleophilic and electrophilic substitution reactions, which make it possible to solve many practical problems in the modification of surfaces to obtain new promising adsorbents, fillers, and thickeners for dispersed media. High-frequency OH stretching vibrations are easily recorded in infrared absorption spectra, and this yields information on the states of systems of OH groups and on the bonds between this system and the substrate. The presence of a rotational degree of freedom and dipole-dipole interaction has appeared experimentally in specific thermoactivation broadening of the spectral infrared absorption lines of OH stretching vibrations in high temperature regions. Additional spectral lines of composite frequencies¹⁰⁻¹² are due to the low-energy spectrum of hindered rotation,¹³ and may lead to orientational cooperative effects.¹⁴ The correlated orientations of dipole moments are the source of strong electric fields, which may affect the adsorbent capacity of the surface.15,16

The issues associated with the reorientations of surface OH groups were examined in earlier publications^{17,18} and led to a number of problems on local and quasi-local vibrations of structurally ordered or disordered systems of dipole radicals, and on orientational phase transitions in two-dimensional dipole systems with full accounting for the longrange and anisotropic dipole-dipole interaction.¹⁹ These problems are topical in other two-dimensional dipole systems, including the dipole heads of phosphorolipidous molecules of biological membranes and dipole organic molecules, which are introduced in van der Waals intervals of stratified inorganic matrices (so-called intercalated compounds).

Actually, it is noted in Ref. 20 that the $P^-...N^+$ dipole of phosphorylcholine has a dipole moment of about 3 D and is oriented parallel to the plane of the two-dimensional lattice (lamellar plane). In this plane there is hindered rotation of the dipole with a rotational correlation time estimated on the basis of the Overhauser effect at $1.4 \cdot 10^{-9}$ s. Intermolecular hydrogen bonds and dipole-dipole interactions may limit the rotational mobility of the dipole, which leads to an orientationally ordered system. The ground state and the spectrum of orientational vibrations of dipoles in a two-dimensional model of a lipid monolayer were calculated in Ref. 21.

References 22-24 are devoted to studies of intercalated semiconductor compounds. In these publications it is shown that in the absence of screening by free electrons, long-range dipole-dipole interaction of introduced molecules leads to a concentration and temperature dependence of the charge transferred from the molecule to the matrix layer. This effect is in many ways analogous to the concentration change in the effective charge of atoms in submonoatomic layers.²⁵ It was predicted in Ref. 22 that it would be possible for several phases to exist in semiconductor intercalated compounds. These phases differ in the period of the superlattice and are characterized by a two-dimensional miniband electron spectrum. This was experimentally proven in Refs. 23 and 24 for compounds of Pb I_2 quinone and Pb I_2 aniline. It is noted in these publications that the mechanism of observed phase transitions may be associated with orientational ordering of the dipole moments of embedded organic molecules. This was theoretically studied in Refs. 26-28. This mechanism is especially likely for the compound PbI₂-aniline because aniline is characterized by a large dipole moment and has in this compound two easy axes of rotation along the P-N and N-C bonds.²⁴

Thus, the theory of orientational states of two-dimen-

sional dipole systems, which was initially developed for surface OH groups, was found to be applicable to a rather broad class of objects. This survey discusses the main results of the theory of vibrations and orientational states in arbitrary two-dimensional dipole systems, and is applied to an explanation of the observed patterns in the most studied two-dimensional dipole system, surface OH groups. For convenience of exposition section 2 presents experimental characteristics of the vibrational and orientational states of this system, which made it possible in subsequent sections to illustrate the theoretical material with corresponding estimates. The logic for the construction of these sections is based on step-by-step inclusion of dipole interaction in the examination of the dipole interaction which forms the orientational conformations of the system and leads to collectivization of vibrational states of individual polar molecules.

Section 3 presents the structure of the vibrational and hindered-rotation spectra of isolated (that is, in the absence of dipole interaction) surface OH groups with analysis of the effect of various perturbations on these spectra. The main results discussed in this section consist of establishing the dominant role of the reorientational mechanism of homogeneous broadening of the spectral lines of molecules with several equilibrium orientations. This differs from the out-ofphase mechanism of anharmonic bonding of stretching vibrational and orientational states, not in a Hamiltonian system, but in a dipole moment operator. In turn, the out-ofphase mechanism considers the anharmonic bond (of order 4) of a high-frequency vibration with degenerate low-frequency librational vibrations of the molecule in a weak exchange of energy with a thermostat.³⁰ This mechanism provides a good description of the one-sided temperature broadening of the spectral lines of complexes with a hydrogen bond observed in various systems.³¹⁻³³ For diatomic groups which have a strong bond of only one heavy atom with a solid matrix, a nontrivial dependence of the temperature shifts of the local oscillation frequencies on the mass of the light atom was obtained. This explains the observed spectral patterns in isotopic exchange.^{34,35}

Section 4 contains an analysis of the orientational ordering of dipoles in various two-dimensional lattices, as well as in a two-dimensional system with random filling of the sites of a lattice of adsorption centers. Here results are presented of calculations of characteristics of the ground states, their stability relative to thermodynamic fluctuations, estimates of the temperatures of orientational phase transitions, areas where paraelectric and ferroelectric phases, and the dipole glass phase exist for a two-dimensional disordered system, with accurate accounting of long-range dipole-dipole interactions. Fundamentally important results of this section are proof of the existence of long-range orientational order in two-dimensional lattice dipole systems^{36,37} and substantiation of the effectiveness of the chain representation of dipole interactions for calculations of the characteristics of the ground state and phase transition temperatures.^{37,38}

After a discussion of the spectral characteristics of isolated dipoles and their orientational conformations, which arise due to dipole-dipole interactions, section 5 discusses dipole renormalization of the vibrational spectra of polar molecules in various orientational phases. Results are presented on dynamic and static renormalizations of the frequencies of stretching and torsional vibrations caused by dynamic and static dipole interactions. The orientational disorder of dipole moments and the disorder of their arrangement on the surface causes an inhomogeneous broadening and asymmetry of the spectral lines.

The last section, section 6, discusses solved and unsolved problems in the theory of two-dimensional dipole systems, interpretation of experimental data, and prospects for future research.

2. INFRARED SPECTROSCOPY OF SURFACE GROUPS OF ATOMS WITH ROTATIONAL DEGREES OF FREEDOM

The main information on vibrational and orientational states of surface groups of atoms is provided by infrared spectroscopy. The volume concentration of these objects needed for measurements ($\sim 10^{20}$ cm⁻³) is obtained in highly dispersed samples with a large specific surface $(\sim 200 \text{ m}^2/\text{g})$. The low-energy orientational states lead to clearly observable temperature dependences of the characteristics of spectral lines of stretching vibrations, and to additional lines of composite frequencies. Reference 29 discusses the results of Refs. 39-42, in which the observed temperature dependences of the line widths of valency vibrations of CO groups in a scaffold position on the surface of Ni(111) and of SiH groups on the surface of Si(100) are linked with low-frequency torsional or flexure vibrations of these objects. These dependences are interpreted on the basis of a three-dimensional out-of-phase model. However, it is shown in section 3 of this article that these and other experimental patterns are described better by a reorientational model of the broadening of spectral lines.¹⁹ To avoid a priori refraction of experimental data through the prism of some model, the authors preferred to present in this section a survey of the experimental characteristics of the vibrational and orientational states of the most studied two-dimensional system of surface OH groups, separately from theoretical interpretations, and to give them a detailed exposition in subsequent sections in the discussion of the results of the corresponding models.

References 4 and 5 present comprehensive experimental material and attention is focused on the classification of OH groups by their arrangement on oxide atoms with various coordinations, by their stability relative to conditions of thermovacuum processing, by their ability to enter some chemical reaction or to change the frequency of vibrations when affected by adsorption agents. In the overwhelming majority of publications the spectra are taken only at room temperatures, and with a resolution which makes it possible to solve the problems listed above. However, these conditions are insufficient to analyze the orientational states. The necessary experimental information on the rotation mobility of surface OH groups can be found in several articles, and we discuss the results of these publications here.

The first infrared absorption spectra with good resolution of the stretching vibrations of OH groups on a dehydrogenated surface of SiO₂ over a wide range of temperatures T = 100-1000 K were obtained in Ref. 9. It was found that the frequency of the maximum of a band ω_{max} (in cm⁻¹) is described with good accuracy by a linear law:

$$\omega_{\max} = 3753,3 \pm 0,2 - (1,74 \pm 0,05) \cdot 10^{-2}T, \qquad (2.1)$$

and the temperature dependence of the half-width of the

band at its half-height $\Delta \omega_{1/2}$ (measured from the perpendicular to the tangent background from the maximum to the high-frequency branch) satisfies Arrhenius' law at T > 400 K:

$$\ln \Delta \omega_{1/2} = 2,10 \pm 0,08 - (442 \pm 35)T^{-1}, \qquad (2.2)$$

from which the value of the rotation activation energy was obtained: $\Delta \varepsilon_{\rm rot} \approx 39$ meV. At T > 400 K, $\Delta \omega_{1/2}$ reaches a constant value $\Delta \omega_{1/2} \approx 2$ cm⁻¹. The number of temperature points for the spectra taken in Ref. 9 was of the order of ten.

Analogous measurements with a large number of temperature points (from 15 to 31 for various samples) at T = 300-800 K for OH and OD groups on a dehydrogenated surface of SiO₂ described in Refs. 17 and 43, yielded the following results:

$$\omega_{\text{max}}^{\text{OH}} = 3753,93 \pm 0,15 - (1,56 \pm 0,05) \cdot 10^{-2}T,$$

$$\omega_{\text{max}}^{\text{OD}} = 2768,82 \pm 0,04 - (1,70 \pm 0,02) \cdot 10^{-2}T,$$
(2.3)

$$\ln \Delta \omega_{1/2}^{OD} = 2,35 \pm 0,03 - (618 \pm 18)T^{-1}.$$
(2.4)

Equation (2.4) occurs at T > 400 K. At T > 600 K these same experimental values of $\Delta \omega_{1/2}$ for OH and OD groups are described well by a linear equation

$$\Delta \omega_{1/2} = (6 \pm 2) \cdot 10^{-3} T^{1,00 \pm 0.05}$$
(2.5)

As an example we present one spectrum recently obtained on a JRS-113V Fourier spectrometer produced by Bruker. The spectrum is of the OH groups of a dehydrogenated SiO₂ surface on which the relaxation of band intensity was recorded at room temperature after holding the sample in vacuum for 50 hours (curves 6 and 7 in Fig. 1).

In addition to the main stretching vibrations of surface OH and OD groups one also observes their overtones. Reference 44 presents the frequencies for the transitions from the ground state of the oscillator to the first (ω_{01}) and second (ω_{02}) excited states. In the case of a SiO₂ surface, these values are

$$\omega_{01}^{\text{OH}} = 3749 \,\text{cm}^{-1}, \quad \omega_{02}^{\text{OH}} = 7326 \,\text{cm}^{-1},$$

$$\omega_{01}^{\text{OD}} = 2761 \,\text{cm}^{-1}, \quad \omega_{02}^{\text{OD}} = 5431 \,\text{cm}^{-1}.$$
(2.6)

In a number of publications, additional wide bands are observed near an intense absorption band at O-H(D)stretching vibrations. References 10 and 11 record the bands at 3650 and 3850 cm⁻¹ for OH groups in silica samples. These bands are about 100 cm⁻¹ from the central band at 3750 cm^{-1} . Bands were also found at 2690 and 2830 cm $^{-1}$, which are 70 cm⁻¹ from the central band at 2760 cm⁻¹ for OD groups. The intensity of high-frequency lateral bands exceeded the intensity of low-frequency bands. These highfrequency components were also observed in Ref. 12 with analysis of their perturbation by various factors: adsorption of CO and immersion of the sample in liquid oxygen and nitrogen. It was found that these perturbations decrease the frequency of stretching vibrations by tens of cm⁻¹, but increased the gap between the high-frequency and central bands by a factor of 1.5-3.5. There was virtually no shift in the band at 38.50 cm^{-1} in the unperturbed sample when the



FIG. 1. Temperature and relaxation changes in the infrared absorption spectrum of OH groups on a dehydrogenated surface of highly dispersed silica after 50 hours in vacuum (10^{-1} mm Hg). *1*. 780 °C; *2*. 720 °C; *3*. 470 °C; *4*. 360 °C; *5*. 140 °C; *6*. 25 °C; *7*. 20 °C.

temperature was dropped to 77 K. When cooled by liquid helium, cuvettes with a SiO₂ sample in a mixture of helium and hydrogen shifted by 30 cm⁻¹ toward the high frequencies.¹² In the case of adsorption of water at the low-frequency shoulder of the 3750 cm⁻¹ band, an additional small peak was observed^{45,46} at 3740 cm⁻¹.

In virtually all observed spectra, the 3750 cm^{-1} band is asymmetrical. The asymmetry increases as the temperature at which the spectrum is taken decreases. The band appears in the slope of the low-frequency shoulder (see, for example, the spectra in Ref. 9 or in Fig. 1). In Refs. 47–49 the shape of this band is described well by artificial separation of the band into three component Lorentzian lines.

The infrared absorption spectra of highly dispersed silica with surface OH groups contain a set of peaks in the longwavelength region at 100–300 cm⁻¹ (Fig. 2). In Ref. 50 a peak was observed at 150 cm⁻¹. In the spectra of inelastic scattering of neutrons on silica gels bands with centers at 300, 200, and 80 cm⁻¹ were also observed.⁵¹



FIG. 2. Long-wavelength infrared absorption spectrum of dehydrogenated highly dispersed silica relative to the tangential background (temperature 20 °C, vacuum 10^{-1} mm Hg).

The distribution of OH groups on the surface of SiO₂ is determined by the fact that they may bond only with every other surface atom of silicon, which are separated by 5 Å and form a likeness of a two-dimensional triangular lattice.⁵²⁻⁵⁴ If every other surface atom of Si does not contain an OH group, the average distance between successive ones will exceed 5 Å. Thus, according to data in Ref. 53, the average distance between OH groups is 6–7 Å, which corresponds to the following probability C of filling of a surface atom of silicon: C = 0.5-0.7. Here we digress from the possibility (discussed in Ref. 55) of the existence of double OH groups on one atom of silicon, with distances between groups of less than 3 Å. The dipole moment of an OH group on a SiO₂ surface was estimated⁵⁶ to be 2.5 D.

The infrared absorption spectra in the region of the stretching vibration frequencies of OH and OD groups on an Al_2O_3 surface exhibit a set of spectral lines: 3700, 3733, 3744, 3780, and 3800 cm⁻¹ for OH groups, and 2733, 2759, and 2803 cm⁻¹ for OD groups.⁵⁷ Information about additional spectral lines observed in these frequency ranges, and their interpretation based on the dependences of the frequencies of O-H(D) stretching vibrations on different coordination of aluminum and oxygen atoms is found in the review of Ref. 58.

In addition to infrared spectroscopy data, dielectric and calorimetric studies are also promising in the study of orientational phase transitions in two-dimensional dipole systems. A survey of the dielectric properties of noncentral ions in KCl:Li, NaBr:F, KCl:OH, and RbCl:OH systems showed² that the volume concentration of these ions, $\sim 3 \cdot 10^{18}$ cm⁻³, is completely sufficient to obtain a temperature dependence of excess permittivity. The use of a double calorimeter to measure the heat capacity of O₂ molecules adsorbed on a graphite surface^{59,60} makes it possible to analyze a system of 10^{21} molecules with a heat capacity resolution of up to 10^{-2} J/K. The volume concentration of surface OH groups in samples of highly dispersed silica reaches 10^{20} cm⁻³, so dielectric and calorimetric studies of these systems should not present special difficulties.

3. STRUCTURE OF VIBRATIONAL AND ORIENTATIONAL STATES OF AN ADSORBED DIATOMIC MOLECULE

Theoretical description of the vibrational and orientational states of adsorbed molecules, independent of the nature of the adsorption bond (physical adsorption with energies less than 0.5 eV, chemical adsorption or the strong chemical bonds of structural groups of surface atoms) in one form or another operate according to a general Hamiltonian system:¹⁹

$$H = H_0 + H_{\rm ph} + H_{\rm int},$$
 (3.1)

in which H_0 are the nuclear degrees of freedom of the adsorbed molecule, H_{ph} are the vibrations of the substrate atoms, and H_{int} is the interaction of the molecule with phonons or the stationary force field of the substrate. The explicit form of the Hamiltonian H_0 depends on the type of adsorption bond. For the case of physical adsorption, one can use a Hamiltonian of a gas phase molecule for H_0 . The quantity H_{int} can be used to describe the perturbations introduced in adsorption. For example, in Ref. 61, H_0 included the rotational degrees of freedom of a diatomic molecule, and H_{int} formed the potentials outside and inside the planar hindered rotations arising in physical adsorption. The energy spectrum of hindered rotation which was obtained was used for numerical calculations of heat capacity, and the calculations agreed with calorimetric studies.⁶²

For chemosorbed molecules or structural groups of surface atoms, the Hamiltonian H_0 should include the effective force field of substrate atoms fixed in equilibrium conditions. The quantity H_{int} should include interaction with corresponding shifts. Let us examine the structure of the vibrational and orientational states of an OH group strongly bound by an oxygen atom to a surface atom, forming an oxide.¹⁹ The equilibrium positions of the hydrogen atom are defined by the radial distance $r_0 \approx 1$ Å relative to the oxygen atom, by the polar angle $\theta_0 \approx 90^\circ$ reckoned from the normal to the surface, and by several values of the azimuthal angle $\varphi_j = \varphi_0 + (2\pi j/n)$, where j = 1,...,n, n is the number of symmetrically arranged neighboring atoms of oxygen in the substrate. Rather rigid fixing of a hydrogen atom relative to variables r and θ is combined with hindered rotation in the plane of the surface, which is described by variable φ . Due to the small mass $m_{\rm H}$ of the hydrogen atom, its movement parameters differ greatly from the characteristics of other atoms in the system. A one-particle Hamiltonian H_0 in a harmonic approximation of stretching and deformational vibrations acquires the form¹⁷⁻¹⁹

$$H_0 = -\frac{\hbar^2}{2m}\Delta + \frac{1}{2}k_r(r - r_0)^2 + \frac{1}{2}k_\theta(\theta - \theta_0)^2 + U(\varphi), \quad (3.2)$$

where Δ is the Laplace operator, $m = m_{\rm H} m_{\rm O} / (m_{\rm H} + m_{\rm O})$ is the reduced mass of the OH system, and k, and k_{θ} are the corresponding force constants,

$$U(\varphi) = \frac{1}{2} \Delta U_{\varphi} \left\{ 1 - \cos\left[n(\varphi - \varphi_0) \right] \right\}$$
(3.3)

is the n^{th} potential well of hindered rotation with a reorientational energy barrier ΔU_{ω} .

The energy levels of the system in the examined approximation are equidistant sets with gaps $h\omega_r$, $h\omega_\theta$, where $\omega_r = (k_r/m)^{1/2}$, $\omega_\theta = (k_\theta/I)^{1/2}$ are the frequencies of the stretching and deformational vibrations $(I = mr_0^2)$ is the moment of inertia) and the spectrum of hindered rotation $\varepsilon_{f\sigma}$ the characteristic form of which is shown in Fig. 3 and is defined by the value of the reduced barrier $p = \Delta U_{\varphi}/$ $h\omega_{\varphi} = (2I\Delta U_{\varphi})^{1/2}/nh$. At $p \gtrsim 1$, the levels of hindered rotation can be classified by a quantum number f = 0, 1,...,which at the limit $p \gg 1$ describes the levels of the harmonic



FIG. 3. Schematic of the position of low energy levels of the hinderedrotation spectrum and allowed dipole transitions (additional transitions with regard to the case n = 2 value of $\sigma = -1$ and the transition marked by a dashed arrow arises at n = 3).

oscillator $\varepsilon_f = h\omega_{\varphi} (f + 1/2)$ with a frequency of torsional vibrations $\omega_{\varphi} = n (\Delta U_{\varphi}/2I)^{1/2}$ and an integral translation quantum number σ with a main region of *n* values: $-n/2 < \sigma \le n/2$. The lowest energy levels are split into the value

$$\Delta \varepsilon_0 \approx \kappa(n) \frac{n^2 \hbar^2}{\pi I} e^{1/2} 2^{5/2} p^{3/2} e^{-4p},$$

$$\kappa(n) = \begin{cases} 1, & n - \text{even} \\ 3/4, & n = 3, \end{cases}$$
(3.4)

while the frequency of transition from the group of levels f = 0 to f = 1 is approximately equal to

$$\omega_{10} \approx \omega_{\varphi} [1 - (4p)^{-1} - (4p)^{-2}]. \tag{3.5}$$

In the opposite limit case $(p \leq 1)$ we have the spectrum of a planar free rotator $\varepsilon_{\alpha} = h^2 \alpha^2 / 2I$, $\alpha = 0, \pm 1, ...$

The shape of the infrared absorption spectral lines is determined by the frequency dependence of the imaginary part of the system polarizability tensor, which is expressed by a commutator of Cartesian components of dipole moment operators averaged over a Gibbs distribution at different times. The vector of the dipole moment $\vec{\mu}$ of an isolated surface OH group can be written as the product of the effective charge q and radius vector r from oxygen atom to hydrogen atom. Then, all spectral characteristics of the isolated OH group will define a retarded Green's function⁶³

$$g^{\alpha\beta}(t) = -\frac{i}{\hbar}\theta(t)\langle [\hat{r}^{\alpha}(t), \hat{r}^{\beta}(0)] \rangle, \quad \alpha, \beta = x, y, z, \qquad (3.6)$$

where $\theta(t)$ is a theta function equal to 1 at t > 0 and 0 at t > 0. Expanding the vector **r** in terms of the stretching Δr and deformation $\Delta \theta$ shifts we obtain:

$$\mathbf{r} = (\mathbf{r}_0 + \Delta \mathbf{r})\mathbf{e}_{\varphi} - (\mathbf{r}_0 + \Delta \mathbf{r})\Delta\theta\mathbf{k}_z, \qquad (3.7)$$

where $\mathbf{k}_z = (0,0,1)$ and $\mathbf{e}_{\varphi} = (\cos\varphi, \sin\varphi, 0)$ is the unit vector of the orientation of an OH group in the surface plane. The desired Green's function can be expressed by the Green's function of the stretching deformational, and hindered-rotation states, which are defined analogous to Eq. (3.6) with substitutions of \mathbf{r} for Δr , $\Delta \theta$, and \mathbf{e}_{φ} . As a result, the spectral lines of deformational and composite stretching deformational vibrations at $\omega_r > \omega_{\theta}$ will be proportional to

 $\operatorname{Im} g^{zz}(\omega) =$

$$-\frac{\pi}{2m\omega_{\theta}}\left\{\delta(\omega-\omega_{\theta})+\frac{\omega_{\text{rot}}}{\omega_{r}}\frac{1-e^{-\hbar\omega/T}}{(1-e^{-\hbar\omega_{r}/T})(1-e^{-\hbar\omega_{\theta}/T})}\times\left[\delta(\omega-\omega_{r}-\omega_{\theta})+e^{-\hbar\omega_{\theta}/T}\delta(\omega-\omega_{r}+\omega_{\theta})\right]\right\},$$

(3.8)

where $\omega_{\text{rot}} \equiv h/(2I)$ is the quantum frequency of free rotation. Here and below, with the exception of numerical estimates, the temperature T will be measured in energy units.

The long-wavelength infrared absorption spectrum is proportional to the imaginary part of the Green's function of hindered rotation:

$$\operatorname{Im} g_{\varphi}^{\alpha\beta}(\omega) = -\frac{\pi}{\hbar} \sum_{f\sigma, f\sigma'} \rho_{f\sigma}(T) \langle f\sigma | \hat{e}_{\varphi}^{\alpha} | f'\sigma' \rangle$$
$$\times \langle f'\sigma' | \hat{e}_{\varphi}^{\beta} | f\sigma \rangle (1 - e^{-\hbar\omega_{f\sigma',f\sigma'}/T}) \delta(\omega - \omega_{f'\sigma',f\sigma})$$

$$\approx -\frac{\pi \Delta \omega_{0}}{T} e^{\alpha} e^{\beta} \delta(\omega - \Delta \omega_{0}) -\frac{\pi}{\hbar} \frac{\omega_{\text{rot}}}{\omega_{\varphi}} e^{\alpha}_{\perp} e^{\beta}_{\perp} [\delta(\omega - \omega_{\varphi}) - \delta(\omega + \omega_{\varphi})];$$
(3.9)

$$\begin{aligned} \alpha, \beta &= x, y, \quad \omega_{f\sigma', f\sigma} = (\varepsilon_{f\sigma'} - \varepsilon_{f\sigma})/\hbar, \\ \rho_{f\sigma}(T) &= e^{-\varepsilon_{f\sigma}/T} / \sum_{f\sigma} e^{-\varepsilon_{f\sigma}/T} \end{aligned}$$

The approximate expression in Eq. (3.9) describes the most intense bands with frequencies $\Delta \omega_0$ and $\omega_{10} \approx \omega_{\varphi}$ (see Fig. 3), which also appear in the region of valency vibrational frequencies:

$$\operatorname{Im} g^{\alpha\beta}(\omega) \approx -\frac{\pi}{2m\omega_{r}} \left\{ e^{\alpha} e^{\beta} \delta(\omega - \omega_{r}) + \frac{\omega_{rot}}{\omega_{\varphi}} e^{\alpha}_{\perp} e^{\beta}_{\perp} \frac{1 - e^{-\hbar\omega/T}}{(1 - e^{-\hbar\omega_{r}/T})(1 - e^{-\hbar\omega_{\varphi}/T})} \times \left[\delta(\omega - \omega_{r} - \omega_{\varphi}) + e^{-\hbar\omega_{\varphi}/T} \delta(\omega - \omega_{r} + \omega_{\varphi}) \right] \right\},$$

$$\alpha, \beta = x, y.$$
(3.10)

The unit vectors \mathbf{e} and \mathbf{e}_{\perp} in Eqs. (3.9) and (3.10) are oriented in the surface plane along and transverse to the equilibrium O-H bond.

Equations (3.8)–(3.10) define the general structure of the bands of infrared absorption of a surface OH group. Since $\omega_r \sim 3750 > \omega_{\theta} \sim 1000 > \omega_{\varphi} \sim 200 \gg \omega_{rot} \sim 20 \text{ cm}^{-1}$, at room temperatures $h\omega_{\varphi} \sim T$. In addition to the main bands at frequencies ω_r , ω_{θ} , and ω_{φ} , one should also observe less intense bands at composite frequencies $\omega_r + \omega_{\theta}$ and $\omega_r + \omega_{\varphi}$, which were recorded¹² for OH(D) groups on the surface of SiO₂ and at frequency^{10,11} $\omega_r - \omega_{\varphi}$ with an intensity which depends strongly on temperature.

Using the unapproximated expression in Eq. (3.9) for the spectrum of hindered rotation, one can verify that the band at frequency ω_r has a fine structure of spectral lines shifted by the tunnel splitting value $\Delta \varepsilon_0 / h$ (see Eq. (3.4)). Resolution of this fine structure depends on the width of the corresponding spectral lines. The same is true of the composite frequencies $\omega_r \pm \omega_{\varphi}$ due to the set of dipole transitions grouped in the spectrum of hindered rotation near frequency ω_{φ} .

The first calculations of the hindered-rotation spectrum for OH groups on the surface of SiO₂ were done in Ref. 13. Table I indicates the values of the frequencies of allowed transitions between low levels shown in Fig. 3 for various values of the reorientation barriers of OH and OD groups for n = 2 and 3. Asterisks mark barrier values for Al₂O₃ and SiO₂ substrates, for which the following observed transition frequencies were obtained: 3700, 3733, 3744, 3780, and 3800 cm⁻¹ for OH groups, and 2733, 2759, and 2803 cm⁻¹ for OD groups on a surface of Al₂O₃ (n = 2). The quantum-chemical calculation of the barrier⁶⁵ also coincides: $\Delta U_{\varphi} = 54.7$ meV for a SiO₂ (n = 3) surface. There is also a correspondence with the rotational activation energy $\Delta \varepsilon_{\rm rot} \approx \Delta U_{\varphi} - (h\omega_{\varphi}/2) \approx 39$ meV found in Ref. 9. The quantity $\Delta U_{\varphi} \approx 54.7$ meV corresponds to the frequency of torsional vibrations $\omega_{11,01}^{\rm OH} \approx 208$ cm⁻¹, $\omega_{11,01}^{\rm OD} \approx 171$ cm⁻¹,

TABLE I. Values of the reorientation energy barriers ΔU_{φ} and corresponding frequencies ω_{10} , $\Delta\omega_0$, $\Delta\omega_1$ of allowed dipole transitions (see Fig. 3) for OH and OD groups in two-well (n = 2) and three-well (n = 3) azimuthal potentials (Eq. (3.3)) for $I_{\rm OH} = 1.48 \cdot 10^{-40}$ g·cm², $I_{\rm OD} = 2.80 \cdot 10^{-40}$ g·cm² (Refs. 13, 19, 64) $(p = (2I_{\rm OH(D)} \Delta U_{\varphi})^{1/2}/nh$ is the reduced barrier).

p	OH groups				OD groups			
	Δ <i>U</i> ,	ω ₁₀ ,	Δω ₀ ,	Δω ₁ ,	ΔU_{u} ,	ω ₁₀ ,	$\Delta \omega_0$,	Δω ₁ ,
	meV	cm ⁻¹	<u>cm</u> -1	cm ⁻¹	meV	cm ⁻¹	cm ⁻¹	cm ⁻¹
n = 2:								
0	0	18,9	18,9	56,7	0	10,0	10,0	30,0
0,707	4,70	30,0	11,2	46,7	2,48	15,9	5,92	24,7
1,118	11,75*	51,1	4,99	34,9	6,21	27,0	2,64	18,4
1,541	22,4	83,6	1,96	21,2	11,78*	44,2	1,04	11,2
2,236	47,0	1 45	0,19	4,56	24,8	76,5	0,10	2,41
n - 3:								
0	0	75,6	18,9	94,5	0	40,0	10,0	50,0
0,745	11,7	88,9	14,9	-	6,2	47,0	7,9	
1,246	32,8	146	5,9	_	17,3	77,3	3,1	
1,610	54,7*	210	2,2	32,9	28,9	111	1,2	-
2,210	103,2	324	0,34	_	54,6*	171	0,18	4,4

while the experimental values^{11,12} are approximately equal to 100 and 75 cm⁻¹. This divergence is removed when one considers the shift in frequencies due to dipole-dipole interaction⁶⁶ (see section 5).

One should also consider the fact that the frequencies ω_{φ} of torsional vibrations of surface OH(D) groups fall in an area of the continuous spectrum of acoustic vibrations of substrate atoms. Thus, these torsional vibrations are quasilocal, and the corresponding unit-normalized spectral function of the square of the frequency has a nonzero width even in the harmonic approximation:¹⁹

 $S(\omega^2)$

$$=\frac{M^2\omega^4}{m(m+M)\omega_{\varphi}^4}\frac{\rho_{\rm S}(\omega^2)}{\left(\frac{M}{m}\frac{\omega^2-\omega_{\varphi}^2}{\omega_{\varphi}^2}-\omega^2 P_{\rm S}(\omega^2)\right)^2+\left(\pi\omega^2\rho_{\rm S}(\omega^2)\right)^2},$$
(3.11)

here *M* is the effective mass of an elementary cell of a crystal containing an extrinsic group with reduced mass *m*, and $\rho_S(\omega^2)$ is the distribution function of the squares of frequencies (density of states) of substrate phonons. The function $P_S(\omega^2)$ is expressed through $\rho_S(\omega^2)$ in the following way:

$$P_{S}(\omega^{2}) = \int_{0}^{\infty} \frac{\rho_{S}(\widetilde{\omega}^{2}) d\widetilde{\omega}^{2}}{\omega^{2} - \widetilde{\omega}^{2}}.$$
(3.12)

In the Debye approximation

$$\rho_{S}(\omega^{2}) = \frac{3\omega}{2\omega_{D}^{3}}\theta(\omega_{D} - \omega),$$

$$P_{S}(\omega^{2}) = \frac{3}{\omega_{D}^{2}} \left(\frac{1}{2}\frac{\omega}{\omega_{D}}\ln\left|\frac{\omega_{D} + \omega}{\omega_{D} - \omega}\right| - 1\right)$$
(3.13)

at $\omega_{\varphi} \ll \omega_{\rm D}$ ($\omega_{\rm D}$ is the Debye frequency) we obtain the following asymptotic behavior for the maximum and half-width of the spectral line of quasi-local vibrations:¹⁹

$$\omega^{2} \approx \omega_{\varphi}^{2} \left(1 - \frac{m}{M} \frac{\omega_{\varphi}^{2}}{\omega_{D}^{2}}\right), \quad \Delta \omega_{1/2} \approx \frac{3\pi}{4} \frac{m(m+M)}{M^{2}} \left(\frac{\omega_{\varphi}}{\omega_{D}}\right)^{3} \omega_{\varphi},$$
(3.14)

that is, the spectral line has a small half-width and is near ω_{ω} .

In the region of frequencies $0.2 < \omega/\omega_D < 1$ the function $P(\omega^2)$, in silicon, for example, undergoes a number of sharp breaks with a rather large amplitude of the change in the function, due to which several quasi-local vibration frequencies may arise.⁶⁷ An analogous situation may also be realized for a real spectrum of surface vibrations in the area of frequencies near the Debye frequency, which explains the set of easily distinguished peaks in Fig. 2 in the 200–300 cm⁻¹ region.

A homogeneous broadening of high-frequency spectral lines of stretching vibrations of isolated OH(D) groups may be associated with the anharmonic decay of the high-frequency excitation of 5–7 low-frequency substrate phonons;⁶⁸ however, the calculated broadening is extremely small and may not be observed. Another broadening mechanism is associated with a stochastic process of reorientation of OH(D) groups, which is examined with different levels of rigor in Refs. 14, 17, 43, and 69. We present the most rigorous result of Ref. 69, in which it is shown that d'Alambert inertial forces due to phonon bursts of the substrate have the primary effect on reorientation. The desired rate of reorientation is defined by the expression

$$w \approx \frac{m\omega_{\varphi}^{4}}{4\pi\rho c^{3}} [\exp(\hbar\omega_{\varphi}T^{-1}) - 1]^{-1}, \qquad (3.15)$$

where for OH groups on a SiO₂ surface, $m \simeq 1.67 \cdot 10^{-24}$ g is the mass of a reorienting atom, $\omega_{\varphi} \simeq 3.77 \cdot 10^{13}$ s⁻¹ (200 cm⁻¹) is the frequency of torsional vibrations, $\rho \simeq 2.2$ g/cm³ is the density of substrate material, $c \simeq 5.6 \cdot 10^5$ cm/s is the average speed of sound. Identification of the probability of transition into the first excited state of torsional vibrations with the rate of reorientations, which is actually represented by Eq. (3.15), is explained by the fact that for a given system $h\omega_{\varphi} \sim \Delta U_{\varphi}$ and the examined transition is accompanied by reorientations. In the region of room temperatures, $w(T) \propto \exp(-h\omega_{\varphi}/T)$, which agrees with the experimental equations (2.2) and (2.4). At $T \ge h\omega_{\varphi}/k_{\rm B} \approx 288$ K $w(T) \sim 10^{-2}$ cm⁻¹ T, and we obtain the experimental equation (2.5). For the values of parameters taken in Eq. (3.15) and for T = 300 K we obtain the theoretical value $w \approx 4.4 \cdot 10^{11}$ s⁻¹ (2.3 cm⁻¹), which agrees well in order of magnitude with the experimental value $2\Delta\omega_{1/2} \approx 3.0 \pm 0.4$ cm⁻¹.

In the region of low temperatures $(k_{\rm B}T \sim \Delta \varepsilon_0 \ll h\omega_{\omega})$ reorientation becomes a quantum (wave) process in which the main role is played by transitions between low tunnelsplit levels in the phonon field of the substrate (tunnel relaxation in a phonon field⁷⁰). In Ref. 19 it is shown that for the systems examined here one-phonon relaxation is realized at $T < T^* \sim 30$ K, and two-phonon relaxation at $T^* < T < T^{**} \sim 170$ K, while at $T > T^{**}$ the thermoactivation mechanism begins to dominate (Eq. (3.15)). Broadening of spectral lines of surface OH groups due to tunnel relaxation ($\sim 10^{-7}$ cm⁻¹ at $T = T^*$) is many orders of magnitude less than $\Delta \varepsilon_0 / h$, and this broadening mechanism is negligibly small compared to inhomogeneous broadening by static electric fields in disordered systems of dipoles (see Sec. 5).

Let us now focus on the fact that the reorientation mechanism of broadening, which is due to the relation between vibrational and orientational variables in the dipole moment operator, is not accompanied by out-of-phase valency vibration, which is examined in Refs. 29, 39-42. Thus, Eq. (3.15) can be written in the following form for the full width of the spectral line: $w = \eta n(\omega_{\varphi}), \eta = 2\Delta\omega_{1/2} (\Delta\omega_{1/2})$ is given by Eq. (3.14) and $n(\omega_{\omega})$ is a temperature-dependent factor of Bose-Einstein statistics which enters into Eq. (3.15)). This differs from the result of the out-of-phase model $w = 2(\delta \omega)^2 n(\omega_{\varphi}) + 1) \eta^{-1}$ which holds true²⁹ for $\eta \ge \delta \omega$, where $\delta \omega$ is the coefficient of an anharmonic fourth order connection between valency and torsional vibrations. It is interesting that the estimates of parameters presented in Ref. 39 $\delta\omega \sim 1$ cm⁻¹, $\eta \sim 30$ cm⁻¹ for CO groups in a scaffold position on a Ni(111) surface cannot satisfy the observed broadening $w \sim 10$ cm⁻¹ of the spectral lines of CO vibrations, which are described well by approximately the same values $\delta\omega \sim \eta \sim 30$ cm⁻¹ with $\omega_{\omega} \approx 220$ cm⁻¹ (Refs. 39-41). At $\delta \omega \sim \eta$ the reduced result of the out-of-phase model (which holds true only for $\eta \ge \delta \omega$), which is accurate except for the cofactor $n(\omega_{\varphi}) + 1 \sim 1$, goes over into Eq. (3.15) for a reorientational broadening mechanism. If we consider that the experimental points in the temperature region 100-300 K can be described by factors $n(\omega_{\omega})$ and $n(\omega_{\omega})(n(\omega_{\omega})+1)$ with equal success, then the broadening of bands of CO and SiH stretching vibrations observed in Refs. 39-42 are apparently exactly the same as for OH vibrations^{9,17,43} associated with the reorientations of the studied objects. This mechanism is characterized by only one parameter, η , and the estimates of this parameter agree well with experimental data.

The out-of-phase broadening mechanism becomes dominant when the coefficient of anharmonicity $\delta \omega$ substantially exceeds the energy exchange η of low-frequency modes of the object with thermostat phonons. This situation is realized for various complexes with hydrogen bonds in which the high-frequency (ω_r) oscillation is anharmonically linked with several degenerate (with multiplicity $l \sim 4$) librational modes of the low frequency ω_{φ} . As a result, one observes a strong one-sided temperature broadening in which the one-sided shift in the maximum of the band is proportional to its width, and at sufficiently high temperatures $(T > h\omega_{\varphi})$, the shift increases linearly with temperature.³¹⁻³³ The shape of the one-sided broadened band of a complex with a hydrogen bond is described by the following spectral function:³⁰

$$S(\omega) = \frac{\omega_{\varphi}}{(l-1)! |\delta\omega| T} \ \theta(z) z^{l-1} e^{-z}, \quad z = \frac{\omega_{\varphi}}{\delta\omega T} (\omega - \omega_r).$$
(3.16)

Equation (3.16), in addition to the linear law for the increase of the width of the band with temperature and a shift in its maximum of the order of 100 cm^{-1} , gives yet another coefficient of proportionality between them. The coefficient was found experimentally in Refs. 31 and 32, and is equal to 1.4 at l = 4. When the energy exchange η increases, the band constricts. This agrees with the results of a phenomenological model of random frequency modulation.^{71,72}

The potential of OH(D) stretching vibrations is approximated well by the model of a Morse oscillator⁴⁴ making it possible to link the force constant k, and the coefficients of anharmonicity α_r , β_r in the expansion

$$U(r) = U(r_0) + \frac{1}{2}k_r(r - r_0)^2 - \frac{1}{3}\alpha_r(r - r_0)^3 + \frac{1}{4}\beta_r(r - r_0)^4$$
(3.17)

with the experimentally measured transition frequencies^{34,73} (Eq. (2.6)):

$$k_{r} = m(3\omega_{01} - \omega_{02})^{2} \approx 858 \text{ N/m},$$

$$\alpha_{r} = \frac{3}{2}k_{r}[m\hbar^{-1}(2\omega_{01} - \omega_{02})]^{1/2} \approx 2,83 \cdot 10^{13} \text{ N/m}^{2},$$

$$\beta_{r} = \frac{7}{6}k_{r}m\hbar^{-1}(2\omega_{01} - \omega_{02}) \approx 4,84 \cdot 10^{23} \text{ N/m}^{3},$$

$$U(r_{0}) = \frac{9}{8}\frac{k_{r}^{3}}{\alpha_{r}^{2}} = \frac{7}{12}\frac{k_{r}^{2}}{\beta_{r}} \approx 5,55 \text{ eV}.$$
(3.18)

Due to the cubic anharmonicity of α_r , the frequency of vibrations is dependent on the external electric field E applied to an oscillator with a static dipole moment $\vec{\mu}$ (Stark vibration effect⁷⁴):

$$\widetilde{\omega}_r \approx \left[1 - (\alpha_r \mu E / r_0 k_r^2)\right] \omega_r. \tag{3.19}$$

If the dipole oscillator has a reorientation degree of freedom, the orientation of $\vec{\mu}$ along vector **E** is energetically favorable in a perturbing electric field **E**. The average value of the cosine of angle φ between vectors $\vec{\mu}$ and **E**, considering the interaction with the substrate thermostat, yields the equation¹⁴

$$\overline{\cos \varphi} = I_1(z)/I_0(z), \quad z = \mu E/T,$$
 (3.20)

where $I_0(z)$ and $I_1(z)$ are Bessel functions of imaginary argument of the first type. The quantity $\cos \varphi$ in Eq. (3.20) is positive; thus, the perturbation of a reorienting group de-

creases (according to Eq. (3.19)) the frequency of stretching vibrations.

On the other hand, the same perturbation should increase the frequency of torsional vibration

$$\widetilde{\omega}_{\varphi} \approx \left[\omega_{\varphi}^{2} + \left(\mu E/I\right)\right]^{1/2}.$$
(3.21)

These ideas, which were presented in Ref. 73, explained the patterns observed in Ref. 12 in the shifts of infrared absorption bands of OH(D) groups on a SiO₂ surface for various perturbations. We note that according to the results of Ref. 64, these very perturbations greatly distort the lateral spectral lines at frequencies $\omega_r \pm \Delta \varepsilon_0 / h$ and may lead to a lack of spectral resolution of the fine structure of the band at ω_r .

To interpret the linear temperature dependences (Eqs. (2.1) and (2.3)) of the frequencies of OH(D) stretching vibrations, Refs. 34 and 35 examined a model of a diatomic anharmonic oscillator (with the potential of Eq. (3.17) and atomic masses m_1 and m_2) bound to the substrate with potentials U_1 and U_2 (Fig. 4). In the limit case $U_1, U_2 \ll U$, $\omega_D \ll \omega_r$, and at $T \gtrsim h\omega_D$, the relation $\omega_r(T)$ is linear and determined by the parameters in Eq. (3.18), by the masses m_1 and m_2 , and by the ratio of the binding energies of the two atoms with the substrate $\varkappa \equiv U_2/U_1$. The relation contains an average over the inverse squares of the frequencies $\langle \omega_r^{-2}(\mathbf{q}) \rangle$ of the phonon spectrum of the substrate:

$$\frac{d\omega_r}{dT} \simeq -\frac{9(k_r/m_1)^{1/2}}{8U(r_0)}\gamma(\gamma - \frac{7}{9})\frac{\varepsilon^{-1/2}(\varkappa + \varepsilon^2)}{(1+\varepsilon)^{3/2}(1+\varkappa)},$$

$$\varepsilon = \frac{m_2}{m_1}, \quad \gamma \approx \omega_D^2 \langle \omega_\nu^{-2}(\mathbf{q}) \rangle = \frac{\omega_D^2}{3N} \sum_{\mathbf{q},\nu} \frac{1}{\omega_\nu^2(\mathbf{q})} \approx 3.$$
(3.22)

Numerical estimation of parameter γ corresponds to the Debye approximation for acoustic vibrations of a crystal.

In Eq. (3.22) there are two contributions which are proportional to $\kappa \varepsilon^{-1/2}$ and $\varepsilon^{3/2}$. The first is associated with the direct effect of substrate phonons on atom m_2 , and thus decreases as m_2 increases. At $\varepsilon \ll 1$ and $\varkappa \sim 1$, the first contribution is dominant. The second contribution arises due to the d'Alambert force of inertia acting on atom m_2 in the noninertial reference frame of atom m_1 , which is subjected to phonon bursts.⁶⁹ It increases as m_2 increases, due to a corresponding increase in the d'Alabmert force. This leads to an intensification of the indirect effect of phonons on m_2 . For an OH(D) system bound to the substrate through an oxygen atom, $x \sim 0.01 \ll 1$ ($U_1 \sim 5$ eV is the binding energy of atoms in a solid, $U_2 \sim 0.1 \text{ eV}$ is the van der Waals interaction) and the contributions $x\varepsilon^{-1/2}$ and $\varepsilon^{3/2}$ are almost identical, which yields a weak dependence on ε in experimental values of $d\omega_{\star}/dT$ (Eqs. (2.1) and (2.3) at $\varepsilon = 1/16$ and 1/8.

When one considers the quantities in Eq. (3.18), the



FIG. 4. Model of a diatomic oscillator coupled to a substrate.

dimensional cofactor in Eq. (3.22) is found to be equal to $-0.0166 \text{ cm}^{-1}\text{K}^{-1}$. The two unknown parameters γ and \varkappa may now be found from experimental data in Eqs. (2.1) and (2.3) at $\varepsilon = 1/16$ and 1/8: $\gamma = 4.3 \pm 0.2$, $\varkappa = 0.013 \pm 0.002$, which agrees well with the order estimates. At $\varepsilon = 3/16$, which corresponds to a "heavy" hydroxyl group with tritium, we obtain the predicted estimate:^{34,35} d ω , $dT = -(2.2 \pm 0.3) \cdot 10^{-2} \text{ cm}^{-1}\text{K}^{-1}$.

Reference 75 examined the lifting of degeracy of energy levels of two-dimensional deformation vibrations of the oxygen atom of a surface OH group. The degeneracy is caused by the force field of the substrate. Reference 75 also examined the interaction of the degeneracy with split tunnel levels (Eq. (3.4)) of hindered rotation of the hydrogen atom. The results were used to interpret the observed temperature manifestation of the fine structure of infrared absorption spectral lines of highly dispersed silica at 900–1000 cm⁻¹.

The theoretical ideas about the vibrational and orientational states of an isolated surface OH(D) group presented in this section provide a completely satisfactory description of the available data of infrared spectroscopy. Nonetheless, because the average distance between neighboring OH groups on a SiO₂ surface is 6-7 Å, the energy of their dipole interaction $V = \mu^2/a^3 \sim 10$ meV is of about the same order as the reorientation barrier ΔU_{φ} or the energy $k_{\rm B}T$ at room temperatures, and a consideration of dipole interaction in these systems is necessary even from general considerations.

4. ORIENTATIONAL ORDERING IN TWO-DIMENSIONAL DIPOLE SYSTEMS

The most studied systems in the theory of phase transitions are systems with short-range interactions, which is due to the need to describe the ferromagnetics with an exchange interaction of spins, and with great simplification of the problem using the nearest-neighbor approximation. A twodimensional degenerate system of moments with shortrange Heisenberg interaction has unusual properties. In this system there is no long-range order;⁷⁶ however, there is a transition into a phase with short-range order, called the Berezinskiĭ–Kosterlitz–Thouless phase^{77,78} which is characterized by power-law behavior of the moment correlator due to spin-wave or vortex excitations. The addition of a weak dipole interaction to the strong ferromagnetic interaction stabilizes the long-range order.^{79,80}

Two-dimensional systems in which long-range dipole interaction plays a significant role are interesting from various points of view. First, they differ from two-dimensional degenerate systems with short-range Heisenberg interaction in that they have an orientational long-range order for any two-dimensional Bravais lattices (except a square one).^{36,37} In a disordered system with disordered filling of the lattice sites by dipoles, a two-dimensional phase of dipole glass arises.⁸¹ Second, anisotropic dipole interaction may lead to complex configurations of dipole moments in the ground state at T = 0. These calculations, which are of interest in and of themselves, have been made using various methods in Refs. 21, 27, 28, 66, and 82–87. Third, the discussed systems are part of a rather broad class of objects (dipole radicals with a rotational degree of freedom on the surface of oxides¹⁹ or dipole heads of phosphorolipidous molecules of biological membranes²⁰ introduced into the interstices of intercalated compounds.^{23,24} Vibrational excitations in

these objects have been experimentally observed and their characteristics depend on the type of ordering.

The first step in studying the orientation ordering of two-dimensional dipole systems consists of an analysis of the ground state. If the orientation of rigid dipoles is described by two-dimensional unit vectors \mathbf{e}_r lying in the plane of the lattice, then the ground state corresponds to the minimum of the system Hamiltonian

$$H = \frac{1}{2} \sum_{\mathbf{r},\mathbf{r}'} V^{\alpha\beta}(\mathbf{r} - \mathbf{r}') e^{\alpha}_{\mathbf{r}} e^{\beta}_{\mathbf{r}'}, \qquad (4.1)$$

in which $\mathbf{r} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 (n_1, n_2 = 0, \pm 1, ..., a_1 \le a_2)$ are the sites of a two-dimensional Bravais lattice, and the tensor $V^{\alpha\beta}(\mathbf{r})$, in the case of dipole-dipole interaction, is defined by the equation

$$V^{\alpha\beta}(\mathbf{r}) = V D^{\alpha\beta}\left(\frac{\mathbf{r}}{a_1}\right), \quad V = \frac{\mu^2}{a_1^3}, \quad D^{\alpha\beta}(\mathbf{r}) = \frac{\delta_{\alpha\beta}}{r^3} - 3\frac{r_{\alpha}r_{\beta}}{r^5}$$
(4.2)

(μ is the dipole moment). Here and below twice repeated Greek superscripts α , $\beta = x$, y of the Cartesian coordinate axes indicate summation. The total energy and the periodic structure of the orientations of N dipoles in the ground state are defined by the equations:^{38,88}

$$H = \frac{1}{2}N\widetilde{V}_{1}, \quad \mathbf{e}_{\mathbf{r}} = \vec{\xi}_{1}^{*}(\mathbf{r}),$$

$$\vec{\xi}_{j}^{*}(\mathbf{r}) = \sum_{l=1}^{L} C_{jl} \widetilde{\vec{\xi}}_{j}(\mathbf{k}_{l}) \exp(i\mathbf{k}_{l}\mathbf{r}),$$

$$\sum_{l=1}^{L} |C_{jl}|^{2} = 1, \quad j = 1, 2,$$

$$(4.3)$$

here $\tilde{V}_1 = \min \tilde{V}_1(\mathbf{k})$, where $\tilde{V}_j(\mathbf{k})$ (with $V_1(\mathbf{k}) \leq \tilde{V}_2(\mathbf{k})$) and $\tilde{\xi}_j(\mathbf{k})$ are the eigenvalues and vectors of the Fourier components of the tensor of dipole interaction:

$$\widetilde{V}^{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{r}} V^{\alpha\beta}(\mathbf{r})\cos(\mathbf{k}\mathbf{r}),$$

$$(4.4)$$

$$\widetilde{V}^{\alpha\beta}(\mathbf{k})\widetilde{\xi}_{j}^{\beta}(\mathbf{k}) = \widetilde{V}_{j}(\mathbf{k})\widetilde{\xi}_{j}^{\alpha}(\mathbf{k}), \quad \widetilde{\xi}_{j}(\mathbf{k})\widetilde{\xi}_{j'}(-\mathbf{k}) = \delta_{jj'}.$$

The "star" of the L wave vectors \mathbf{k}_i corresponds to the degenerate (at L > 1) minimal eigenvalue $\tilde{V}_1(\mathbf{k}_i)$.

The unit length of all vectors $\xi_1(\mathbf{r})$ for an arbitrary anisotropic interaction significantly limits the possible periodic configurations of dipole moments in the ground state, which, except for multidomain structures, may be only homogeneous, and also with a double or quadruple period of the lattice: $\mathbf{k}_i = \mathbf{h}/2$, $\mathbf{h}/4$, where $\mathbf{h} = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2$ is an arbitrary vector of reciprocal lattice38 the $(\mathbf{a}_i \mathbf{b}_j = 2\pi \delta_{ij}, h_1, h_2 = 0, \pm 1, ...)$. For lattice systems with dipole-dipole interaction the arbitrary minima $V_1(\mathbf{k})$ with $\mathbf{k} \neq \mathbf{h}/2$ are absent and the search for configurations of dipoles in the ground state is sufficiently limited by values $\mathbf{k} = 0$, $\mathbf{b}_1/2$, $\mathbf{b}_2/2$ ($\mathbf{b}_1 + \mathbf{b}_2$)/2. This corresponds to minimization of Eq. (4.1) with respect to the orientations of e_r in four sublattices examined in the two-dimensional analog⁸⁴ of the Luttinger-Tisza method.⁸² The quantities $\tilde{V}_1(\mathbf{k})$, generally speaking, cannot be identical to the four listed vectors $\mathbf{k} = \mathbf{h}/2$. Only two cases are possible: when one of these

quantities is minimal, or (for a lattice with symmetry axes order) above the second two equal values $\widetilde{V}_1(\mathbf{b}_1/2) = \widetilde{V}_1(\mathbf{b}_2/2)$. These considerations show that the Luttinger-Tisza method is burdened by independent minimization variables, while analysis of the values of the Fourier components $V_1(\mathbf{k})$ makes it possible to exclude immediately no less than half of the variables and obtain a result much more quickly. Degeneracy of the ground state occurs either due to coincidence of minimal values of $V_1(\mathbf{k})$ at two boundary points of the first Brillouin zone $\mathbf{k} = \mathbf{b}_1/2$ and $\mathbf{k} = \mathbf{b}_2/2$, or as a result of the equality $V_1(\mathbf{k}) = V_2(\mathbf{k})$ at the same point $\mathbf{k} = \mathbf{h}/2$. The natural consequence of degeneracy of the ground state is the presence of a Goldstone mode in the spectrum of orientational vibrations.88

Let us present the characteristics of the ground states of dipoles (with dipole interaction, Eq. (4.2)) in square, triangular, rectangular, and rhombic lattices. The ground state of a square dipole lattice was first established by the Luttinger-Tisza method in Ref. 84, and by minimization of $\tilde{V}_1(\mathbf{k})$ in Refs. 27 and 28. The energy of this state in the calculation for one dipole is $H_0 = (1/2) \tilde{V}_1(\mathbf{b}_1/2) = (1/2) \tilde{V}_1(\mathbf{b}_2/2) = -2.5495 V$, which is about $\Delta H_0 = 0.291 V$ lower than the energy of the ferroelectric state. The corresponding configurations of dipoles have a microvortex structure with a period 2a and with degeneracy in angle α (Fig. 5a). The expansion of Fourier components of the tensor of dipole interaction near the minimum point at the boundary of the first Brillouin zone, when the Cartesian axes Ox and Oy are respectively chosen along \mathbf{b}_1 and \mathbf{b}_2 (Fig. 5b), has the form

$$\widetilde{D}^{\alpha\beta}(\mathbf{k} + \mathbf{b}_{1}/2) = \begin{pmatrix} 6,033 & 0\\ 0 & -5,099 \end{pmatrix} + \begin{pmatrix} -1,170 & 0\\ 0 & 0,145 \end{pmatrix} q_{x}^{2} \\ + \begin{pmatrix} -1,333 & 0\\ 0 & 1,786 \end{pmatrix} q_{y}^{2} - 0,879 \begin{pmatrix} 0 & 1\\ 1 & 0 \end{pmatrix} q_{x}q_{y},$$
(4.5)



FIG. 5. Ground state for a square lattice of dipoles. a. Orientations of dipole moments; b. wave vectors of the structure in the first Brillouin zone; c. and d. orientations of dipole moments in infinitely small and large external electric fields, respectively.

where $q = ka \ll 1$, $a = a_1 = a_2$, and the expression for $\tilde{D}^{\alpha\beta}(\mathbf{k} + \mathbf{b}_2/2)$ follows from Eq. (4.5) with the substitutions $q_x \leftrightarrow q_y$ and $xx \leftrightarrow yy$ of matrix components. The eigenvectors in Eq. (4.4) and the coefficients C_{jl} in Eq. (4.3) are defined as follows:

$$\widetilde{\xi}_{2}(\mathbf{b}_{1}/2) = \widetilde{\xi}_{1}(\mathbf{b}_{2}/2) = (1, 0), \quad \widetilde{\xi}_{2}(\mathbf{b}_{2}/2) = \widetilde{\xi}_{1}(\mathbf{b}_{1}/2) = (0, 1),$$

$$C_{11} = -C_{21} = \sin \alpha, \quad C_{12} = C_{22} = \cos \alpha.$$
 (4.6)

An infinitely small electric field E at an arbitrary angle $\varphi_{\rm E}$ to the Ox axis removes the degeneracy of the ground state and leads to a stratified (with period 2*a*) structure of dipole orientations along one of the axes of the lattice. This is the largest angle (that is, in the interval from 45 to 90°) with a field vector⁸⁹ (Fig. 5c). In this phase the energy of the ground state is quadratic in the field. When the following approximate equation is satisfied

$$\mu E \approx 2 \frac{1 - \sin \varphi_{\rm E}}{\cos^2 \varphi_{\rm E}} \Delta H_0, \quad 0 \le \varphi_{\rm E} \le 45^{\circ}, \tag{4.7}$$

the system switches to a ferroelectric phase with orientation of the dipoles along the field (Fig. 5d). The energy of the ground state decreases linearly as E increases. The metastable states of this system were studied in Ref. 90. Thus, in contrast to the usual situation, when the external field orients the dipole moments along itself (for example, in ferroelectrics), in this case the perturbing field causes transverse orientations of dipoles along the axes of the lattice. Moreover, sufficiently weak fields $(E \sim \Delta H_0 / \mu \ll H_0 / \mu$ \sim atomic fields) may regulate the abrupt change in the structure of dipole orientations.

The ferroelectric ground state in a triangular lattice with degeneracy along the angle of inclination of the dipoles to the axes of the lattice was established in Refs. 27 and 28. The characteristics of this state are given by the following equations (see also Ref. 66)

$$H_0 = \frac{1}{2} \tilde{V}_1(0) = \frac{1}{2} \tilde{V}_2(0) = -2,7585V,$$

$$\tilde{D}_1(k) \approx -D_0 + 0,2633q^2, \quad \tilde{D}_2(k) \approx -D_0 + (4\pi/\sqrt{3})q,$$
(4.8)

$$D_0 = 5,517, \quad \tilde{\xi}_1(0) = (\cos \alpha, \sin \alpha), \quad \tilde{\xi}_2(0) = (-\sin \alpha, \cos \alpha),$$

$$C_{11} = C_{21} = 1,$$

where $q = ka \ll 1$. The full dependences $\widetilde{D}_j(\mathbf{k})$ along symmetrical directions of the first Brillouin zone for square and triangular dipole lattices were calculated in Ref. 66 and are presented in Fig. 6. In an approximation of the circular (radius $q_m = 3.733$) first Brillouin zone of a triangular lattice, the following analytical expression was obtained:⁶⁶

$$\begin{split} \widetilde{D}_{1}(q,\,\Phi) &= -D_{0}\left(1 - \frac{24}{35}\,\widetilde{q}^{2} - \frac{12}{35}\,\widetilde{q}^{4}\cos\,6\Phi\right),\\ \widetilde{q} &= \frac{q}{q_{m}}, \ \Phi - \text{angle q}, \, Ox, \end{split} \tag{4.9} \\ \widetilde{D}_{2}(q,\,\Phi) &= -D_{0}\left[1 - \frac{24}{5}\,\widetilde{q} + \frac{108}{35}\,\widetilde{q}^{2}(1 + \frac{2}{9}\cos\,6\Phi)\right], \end{split}$$



FIG. 6. Eigenvalues of the Fourier component of the dipole interaction tensor in two-dimensional infinite lattices. The solid lines are for a triangular lattice, the dashed lines are for an analytical approximation (4.9), and the dotted lines are for a square lattice.

which correctly reflects the topology of the surface $\widetilde{D}_j(\mathbf{q})$ and is sufficiently accurate in the long-wavelength region $q \ll 1$ (compare the dashed and solid curves in Fig. 6).

Coincidence of minimal values $\tilde{V}_1(\mathbf{b}_1/2) = \tilde{V}_1(\mathbf{b}_2/2)$ for a square lattice and the satisfaction of the equality $\tilde{V}_1(0) = \tilde{V}_2(0)$ for a triangular lattice leads to degeneracy of the ground states and the emergence of a Goldstone mode in the spectrum of orientational dipole vibrations.^{38,88} If one of the possible configurations of the ground state is chosen to be the configuration of dipole orientations along some lattice axis, then the main contribution to dipole energy is made by intrachain interactions:

$$H_0^{\rm ch} = -2V \sum_{n=1}^{\infty} n^{-3} = -2V\zeta(3) \approx -2,404V, \quad V = \mu^2/a^3,$$
(4.10)

while interchain interactions fall off exponentially as the interchain distance z increases:⁶⁶

$$H_0^{\text{int}} \approx [8\pi^2 V/(z/a)^{1/2}] \exp(-2\pi z/a) \cos(2\pi \Delta a/a), \quad z \ge a,$$

(4.11)

where a is the distance between chain sites, Δa is the shift in sites in neighboring chains. For a triangular lattice $z = (\sqrt{3}/2)a$, $\Delta a = a/2$ and the negative value $H_0^{\text{int}} = -0.354V$ indicates the ferroelectric ordering of dipoles in neighboring chains. For a square lattice z = a, $\Delta a = 0$ we obtain a positive value $H_0^{\text{int}} = 0.146V$, which changes sign in antiferroelectric ordering of dipoles in neighboring chains, which corresponds to the ground state.

Two-dimensional Bravais lattices with axes of symmetry of no greater than second order are characterized by an undegenerate dipole ground state. In a rectangular lattice the dipoles are oriented along the chains with the least intersite distances a_1 with antiferroelectric ordering in neighboring chains. For example, for the rectangular lattice examined in Ref. 21 with $a_2 = \sqrt{3}a_1$, the energy of the ground state is defined with an accuracy of up to 0.1% by intrachain interaction (Eq. (4.10)), because $H_0^{\text{int}} = 10^{-3}V$.

The ground states of rhombic lattices with an arbitrary rhombic angle α were studied using the Luttinger-Tisza method in Ref. 19. A description of these states using a chain



FIG. 7. Configurations of dipole moments in a two-dimensional rhombic lattice.

distribution of interactions (such as Eqs. (4.10) and (4.11)) was presented in Ref. 19. Figure 7 presents different configurations of dipoles which satisfy conditions of periodicity with $\mathbf{k} = \mathbf{h}/2$. The dependences of the corresponding dipole energies H_0/V on the rhombic angle α are given in Fig. 8. At $\alpha \leq 60^{\circ}$ the ground state is a diagonal ferroelectric phase DF with orientation of the dipoles along the minor diagonals of the rhombi (Fig. 7b). The axis line between the phase curves DF and DAF corresponds to the contribution of intrachain interactions $-\zeta(3)/[4\sin^3(\alpha/2)]$. For a triangular lattice $(\alpha = 60^{\circ})$ the values of the energies of phases DF, F, and DF_1 coincide, so the parallel orientations of the dipole moments may form an arbitrary angle with the axes of the lattice. In the range of values $60^{\circ} \le \alpha \le 80^{\circ}$ the ground state is also ferroelectric, but with orientation of the dipole moments along the major diagonals of the rhombi (phase DF_1) in Fig. 7c). Finally, at $80^\circ \leq \alpha \leq 90^\circ$ the antiferroelectric phase AF is favorable in terms of energy (Fig. 7d). Let us turn our attention to the intersection of curves AF and V, as well as DF, F, and DF₁ at point $\alpha = 90^\circ$, which indicates the degeneracy of these groups of states for a symmetrical square lattice.

In the general case of arbitrary two-dimensional Bra-



FIG. 8. Dependences of the dipole energies of various orientation states (see Fig. 7) on the rhombic angle α .

vais lattices (not rectangular and rhombic), the ground state, depending on the lattice parameters (x_0 and y_0 in Fig. 9), is characterized by ferroelectric $(0.25 \le x_0 \le 0.5)$ or bisublattice antiferroelectric stratified ordering $(0 \le x_0 \le 0.25)$. The parallel or antiparallel orientations of dipoles to each other may form certain angles θ_F or θ_A with the Ox axis of the lattice, which is drawn along the chains with the smallest intersite distances³⁸ $(a_1 \leq a_2 \leq |\mathbf{a}_1 - \mathbf{a}_2| \leq |\mathbf{a}_1 + \mathbf{a}_2|)$. The energies of these ground states can also be conveniently calculated in a chain representation with expressions which are somewhat more awkward³⁸ than Eqs. (4.10) and (4.11).

Thus, in studies of the properties of dipole systems, the most fruitful representation is the representation of chain interactions, which, first, reflects the tendency toward ordering of dipole moments along the axes of chains with a small ratio of interchain interactions to intrachain interactions. Second, this type of representation makes it possible to use analytical equations with great accuracy. These equations sum the interaction with all dipoles of the lattice. Third, there are grounds for the use of the generalized approximation of an interchain self-consistent field presented in Refs. 91 and 92 to describe the orientational phase transitions.

Ferroelectric ordering in determinate infinite two-dimensional lattices is due to the long-range contribution of dipole forces. Thus, it is not surprising that in limited twodimensional lattices numerical calculations of dipole inter-



FIG. 9. Two-dimensional Bravais lattice with basis vectors \mathbf{a}_1 , \mathbf{a}_2 , and reciprocal lattice vectors \mathbf{b}_1 , \mathbf{b}_2 . The solid and dashed arrows at angles θ_F and θ_A give the ferroelectric ($\mathbf{k} = 0$) and antiferroelectric ($\mathbf{k} = \mathbf{b}_1/2$) configurations of dipoles in the ground state.

actions lead to the replacement of ferroelectric states with macrovortex states⁸⁵ that are approximated to ferroelectric states far from the center of the limited lattice (coinciding with the center of the macrovortex).

Analysis of the ground states of two-dimensional dipole systems might be a purely methodological problem with no practical value if the thermodynamic fluctuations which arise at infinitely small (but nonzero) temperatures could disrupt the orientational ordering. This situation arises, for example, in a one-dimensional Ising model⁹³ with the interaction $V(r) \propto r^{-3}$. Proof of the stability of the ground state and the existence of long-range order at low temperatures in two-dimensional systems with dipole interaction and arbitrary (degenerate) dipole orientations in the plane of the lattice was presented in Refs. 36 and 37.

Let us decompose the unit vectors of dipole orientation $\mathbf{e}_{\mathbf{r}}$ along the vectors $\vec{\xi}_1(\mathbf{r})$ and $\vec{\xi}_2(\mathbf{r})$ of the ground state, which are defined by Eq. (4.3)

$$\mathbf{e}_{\mathbf{r}} = \vec{\xi}_{1}(\mathbf{r})\cos\varphi_{\mathbf{r}} + \vec{\xi}_{2}(\mathbf{r})\sin\varphi_{\mathbf{r}}.$$
(4.12)

Then the angles φ_r can be seen as fluctuations with respect to the ground state. At low temperatures, φ_r are small, and in a Gaussian approximation of long-wavelength fluctuations of the angular Fourier components $\tilde{\varphi}(\mathbf{k})$, the Hamiltonian of (Eq. (4.1)) is equal to

$$H = \frac{1}{2}N\widetilde{V}_1 + \frac{1}{2}\sum_{\mathbf{k}} J(\mathbf{k})|\widetilde{\varphi}(\mathbf{k})|^2, \qquad (4.13)$$

where

$$J(\mathbf{k}) = \sum_{l=1}^{2} C_{2l}^{2} \widetilde{V}^{\alpha\beta}(\mathbf{k} + \mathbf{h}_{l}/2) \widetilde{\xi}_{2}^{\alpha}(\mathbf{h}_{l}/2) \widetilde{\xi}_{2}^{\beta}(\mathbf{h}_{l}/2) - \widetilde{V}_{1}.$$
(4.14)

In this approximation the parameter of long-range order η acquires the form

$$\eta^{2} = \lim_{r \to \infty} \left\langle \cos(\varphi_{\mathbf{r}_{1}+\mathbf{r}} - \varphi_{\mathbf{r}_{1}}) \right\rangle = \exp(-\frac{T}{N} \sum_{\mathbf{k}} \frac{1}{J(\mathbf{k})})$$
(4.15)

and the presence of long-range order $(\eta \neq 0)$ depends on the convergence of sums over k of $J^{-1}(k)$.

Anisotropic dipole interaction in two-dimensional lattices with a symmetry axis of order no greater than two leads to the fact that the function $J(\mathbf{k})$ does not go to zero at any \mathbf{k} . Actually, in this case in Eq. (4.14) l = 1, $\tilde{V}_2(\mathbf{h}_1/2) > \tilde{V}_1(\mathbf{h}_1/2)$ and

$$J(\mathbf{k}) = \widetilde{V}_1(\mathbf{k} + \mathbf{h}_1/2)\sin^2\alpha_{\mathbf{k}} + \widetilde{V}_2(\mathbf{k} + \mathbf{h}_1/2)\cos^2\alpha_{\mathbf{k}} - \widetilde{V}_1(\mathbf{h}_1/2),$$
(4.16)

where $\alpha_{\mathbf{k}}$ is the angle between the vectors $\tilde{\xi}_2 (\mathbf{k} + \mathbf{h}_1/2)$ and $\tilde{\xi}_2 (\mathbf{h}_1/2)$. At $\mathbf{k} = 0$, $\alpha_{\mathbf{k}} = 0$ and $J(0) = \tilde{V}_2 (\mathbf{h}_1/2) - \tilde{V}_1 (\mathbf{h}_1/2) > 0$. At $\mathbf{k} \neq 0$, due to the inequality $\tilde{V}_2 (\mathbf{k} + \mathbf{h}_1/2) \ge \tilde{V}_1 (\mathbf{k} + \mathbf{h}_1/2) \ge \tilde{V}_1 (\mathbf{h}_1/2)$, we also have $J(\mathbf{k}) > 0$. Thus, at the sites of the examined lattices the dipole interaction forms local potentials (proportional to $(1/2) J_{\min} \varphi_r^2$ at small φ_r), which stabilize the long-range order. One cannot examine the thermodynamics of the transfer of orientations of dipoles at large angles between the local equilibrium positions which are formed, because from the limit case of an exactly solved two-dimensional Ising model with short-range action there should also be long-range order.

If a ferroelectric ground state is realized in a two-dimensional lattice with a symmetry axis of order higher than two (which occurs in a triangular dipole lattice) the longwavelength asymptotic behavior of the tensor $\tilde{V}^{\alpha\beta}(\mathbf{k})$ can be written in the form (see Eq. (4.8))

$$\widetilde{V}^{\alpha\beta}(\mathbf{k}) = \widetilde{V}_1(k)\delta_{\alpha\beta} + (\widetilde{V}_2(k) - \widetilde{V}_1(k))k_{\alpha}k_{\beta}k^{-2}, \qquad (4.17)$$

and, according to Eq. (4.14)

$$J(\mathbf{k}) = \widetilde{V}_1(k) - \widetilde{V}_1 + (\widetilde{V}_2(k) - \widetilde{V}_1(k))(k\widetilde{\xi}_2^{\bullet}(0))^2 k^{-2}.$$
(4.18)

In the approximation of a circular Brillouin zone the desired sum over k in Eq. (4.15), after integration with respect to the angle between k and $\tilde{\xi}_2(0)$, acquires the form³⁶

$$\frac{1}{N} \sum_{\mathbf{k}} \frac{1}{J(\mathbf{k})} \approx \frac{S_0}{2\pi} \int_0^{\infty} \frac{k dk}{\{[\tilde{V}_1(k) - \tilde{V}_1] [\tilde{V}_2(k) - \tilde{V}_1]\}^{1/2}}$$
(4.19)

 $(S_0$ is the area of the elementary cell). An analogous integral arose in Ref. 19 for the correlator component transverse to an external electric field E

$$\langle \varphi_{\mathbf{r}}^{2} \rangle_{\mathcal{C}^{2}} \int_{0}^{m} \frac{k dk}{\{[(\mu E/\eta) + \widetilde{V}_{1}(k) - \widetilde{V}_{1}][(\mu E/\eta) + \widetilde{V}_{2}(k) - \widetilde{V}_{1}]\}^{1/2}}.$$

$$(4.20)$$

For isotropic short-range interactions $\tilde{V}_1(k) = \tilde{V}_2(k) \approx \tilde{V}_1 + \gamma k^2$, and Eq. (4.20) switches to the well-known equation⁹⁴

$$\langle \varphi_r^2 \rangle \propto \int_0^{k_m} \frac{k \mathrm{d}k}{(\mu E/\eta) + \gamma k^2},$$
 (4.21)

proving the absence of long-range order in a two-dimensional system with short-range Heisenberg interaction⁷⁶ (since only as $\eta \rightarrow 0$ can one eliminate the divergence which arises as $E \rightarrow 0$ of the integral in $\langle \varphi_r^2 \rangle$, which is bounded by definition). For $E \rightarrow 0$, and $\eta \neq 0$ the integral in Eq. (4.20) coincides with Eq. (4.19), and its convergence signifies the presence of long-range order.

For a triangular dipole lattice the long-wavelength asymptotic behavior of $\tilde{V}_1(k)$ and $\tilde{V}_2(k)$ is defined by Eq. (4.8). The presence of a linear dependence of $\tilde{V}_2(k)$ after substitution of Eq. (4.8) into Eq. (4.19) leads to the fact that the denominator of the integrand is proportional to $k^{3/2}$, the integral converges, and the ferroelectric ground state is stable^{36,37} ($\eta \neq 0$).

In the case of a square dipole lattice, one must substitute Eqs. (4.5) and (4.6) into the general equation (4.14): J(k)

$$\approx V[1,786(q_x^2 \sin^2 \alpha + q_y^2 \cos^2 \alpha) + 0,145(q_x^2 \cos^2 \alpha + q_y^2 \sin^2 \alpha)].$$
(4.22)

The asymptotic behavior of $J(\mathbf{k})$ in the case of a square lattice leads to a logarithmic divergence of the exponent in Eq. (4.15). Thus, there is no long-range order in this system $(\eta = 0)$, and the correlator $\langle \cos(\varphi_{\mathbf{r}_1 + \mathbf{r}} - \varphi_{\mathbf{r}_1}) \rangle$ depends on a power of r, and at $\alpha = \pi/4$ (see Fig. 5a) the decrease in the correlations of angles is least. The power-law decrease in the correlator is characteristic for a phase with a short-range order of the Berezinskiĭ-Kosterlitz-Thouless type,^{77,78} which should also be realized in a square lattice with degenerate dipole orientations.^{36,37}

Ferromagnetic ordering of two-dimensional systems

with dipole-dipole and exchange interactions in the approximation of a spherical model was examined in Ref. 95. The main simplifying assumption of the spherical model is the replacement of the condition $|\mathbf{e}_r| = 1$ on the orientation vectors with the weaker condition $\Sigma_r \mathbf{e}_r^2 = N$, which leads to incorrect conclusions about the absence of long-range order in two-dimensional dipole systems with a continuously degenerate ferromagnetic ground state (which is indicated in Ref. 37).

Based on an examination of the partition function involving the dipole orientations in the functional of electric fields, which takes into account only the long-wavelength asymptotic behavior $k_{\alpha}k_{\beta}/k^2$ of the dipole interaction tensor in a triangular lattice, and which corresponds to a continuous approximation, Ref. 96 erroneously concluded that long-range order was absent in arbitrary two-dimensional dipole systems. First, the latter are characterized by another long-wavelength asymptotic expression of the type of $k_{\alpha}k_{\beta}/k$, and second, the ground state in these systems can correspond to wave vectors **k** at the boundary of the first Brillouin zone, and in spite of all the elegance of the formalism of field functionals for dipole systems one cannot get around the discrete nature of the lattice.³⁷

The presence of local potentials such as hindered-rotation potentials (Eq. (3.3)) in addition to dipole interactions of (Eq. (4.1)) immediately stabilizes long-range order.^{19,36,37} The limiting case of two or four discrete orientations of dipoles in the plane of the lattice, with a consideration of only nearest-neighbor dipole interactions, makes it possible to reduce the problem of calculating the statistical sum to an exactly solvable two-dimensional Ising model.^{26,27} For example, for a square lattice with two allowed orientations of dipoles along some axis of the lattice, or four orientations along the bisector of angles between the axes ($\alpha = 0$ and $\pi/4$ in Fig. 5a), the transition temperatures will be respectively $T_c = 3.282$ or 1.641V (the difference of a factor of two in these values reflects the transition from a one-dimensional to a two-dimensional orientation space).

The description of phase transitions in a two-dimensional dipole system with exact accounting of long-range dipole interaction and the arbitrary barriers ΔU_{φ} of local potentials (Eq. (3.3)) was presented in Refs. 27 and 28 in an approximation of a self-consistent field. The characteristics of these transitions were found to be dependent on ΔU_{φ} and the number *n* of local potential wells. At n = 2, T_c varies from $|\tilde{V}_1|/2$ to $|\tilde{V}_1|$ as ΔU_{φ} increases from 0 to ∞ . At n = 3 the transition to the ferroelectric phase is a type I transition (in contrast to all other cases with type II transitions). The heat *q* and temperature T_c of the transition vary in the following ranges: q = 0 to $|\tilde{V}_1|/8$, $T_c = (|\tilde{V}_1|/2)$ to $(3|\tilde{V}_1|/8 \ln 2)$ as ΔU_{φ} varies from 0 to ∞ . For $n \ge 4$ and for arbitrary ΔU_{φ} , $T_c = |\tilde{V}_1|/2$, however, the dependence on ΔU_{φ} is still preserved in the coefficient in front of η^4 of the Landau expansion when n = 4.

It is well known that the self-consistent field approximation overestimates the transition temperatures. References 36 and 37 obtained estimates of the lower limit of T_c for a triangular dipole lattice with degenerate orientations $(\Delta U_{\varphi} = 0): T_c > 0.693V$, which is about a factor of four less than the estimate of the self-consistent field approximation, $T_c = 2.7585V$. The lower phase transition temperatures in two-dimensional dipole systems may be explained using a chain representation of interactions (Eqs. (4.10) and (4.11)). The strong intrachain dipole interaction cannot insure long-range order in an isolated chain, so low phase transition temperatures are caused by the small value of interchain interactions. Good estimates of transition temperatures T_c which consider the small value of interchain interactions may be obtained using a generalized approximation of an interchain self-consistent field^{91,92} in which an exact solution of a one-dimensional Ising model with short-range action $H_0^{ch} = -2V$ is used. The quantity T_c is a factor of two smaller for two-dimensional dipoles than for one-dimensional dipoles, so according to Refs. 91 and 92

$$T_{\rm c} \approx \frac{2V}{\ln|H_0^{\rm ch}/H_0^{\rm int}|}.$$
 (4.23)

Substituting herein values of H_0^{int} we obtain really low values $T_c \approx 1.15$ and 0.76V for triangular and square lattices respectively.³⁷ Reference 87 uses the Monte Carlo method to establish the phase transition temperature $T_c \approx 0.75V$ for a square dipole lattice. In the rectangular dipole lattice examined in Ref. 21 with $a_2 = \sqrt{3}3a_1$ the phase transition, according to Eqs. (4.11) and (4.23) occurs at $T_c \approx 0.26V$. For the values of parameters $\mu = 25$ D, $a_1 = 5$ Å taken in Ref. 21, we obtain the estimate $T_c \approx 94$ K. The asymptotic behavior of T_c in lattices with large interchain distances ($z \ge a$) directly follows³⁷ from Eqs. (4.11) and (4.23):

$$T_{\rm c} \approx \frac{1}{\pi} \frac{\mu^2}{a^2 z}.$$
 (4.24)

A full accounting of intrachain interactions, including the contribution of neighbors which are not the nearest neighbors in chains, and interchain interactions, is included in the self-consistent field, and leads to an increase in the transition temperatures in Eqs. (4.23) and (4.24) by a factor³⁸ of $\zeta(2) \approx 1.645$.

Let us turn now to a description of orientational states in spatially-disordered two-dimensional systems of dipoles, that may occupy sites of a triangular lattice of adsorption centers with a probability c. The *T*-c phase diagram for orientational states was examined in Ref. 81 in a simple selfconsistent field approximation, and is presented in Fig. 10. To construct it, the thermodynamic average value of orientation $\langle \mathbf{e}_r \rangle_E = \langle \cos\varphi_r \rangle (\mathbf{E}/E)$ in an external electric field **E**, which is defined by Eq. (3.20), was averaged over random fields acting on a dipole and produced by its disordered neighbors (both near and far):

$$\vec{\eta} \equiv \langle \langle \mathbf{e}_{\mathbf{r}} \rangle_E \rangle = \int d\mathbf{E} P(\mathbf{E}) \langle \mathbf{e}_{\mathbf{r}} \rangle_E,$$
 (4.25)

where $P(\mathbf{E})$ is the distribution function of the random fields. The quantity $\vec{\eta}$ is the long-range order parameter of the ferroelectric phase (F). An analogous average of the square of $\langle \mathbf{e}_r \rangle_E$ defines the order parameter of the dipole glass phase (G):

$$\lambda \equiv \langle \langle \mathbf{e}_{\mathbf{r}} \rangle_{E}^{2} \rangle = \int d\mathbf{E} P(\mathbf{E}) \langle \mathbf{e}_{\mathbf{r}} \rangle_{E}^{2}, \qquad (4.26)$$

in which the orientations of dipoles are "frozen in" and there may be no spontaneous polarization ($\eta = 0$). The transition temperatures from the paraelectric phase (P) to the ferroelectric phase T_F and to the dipole glass phase T_G correspond to infinitely small quantities η and λ , which are linked with



FIG. 10. Phase diagram of orientation states of dipoles, with probability c of filling the sites of a triangular lattice).

the first moments $P(\mathbf{E})$ by the equations

$$\mu \langle \mathbf{E} \rangle = 5,517 V \eta c, \quad \mu^2 \langle \Delta \mathbf{E}^2 \rangle = 15,94 V^2 (\lambda^2 - c\eta^2) c. \quad (4.27)$$

In small fields $\langle \mathbf{e}_r \rangle_E \approx \mu \mathbf{E}/2T$ and from Eqs. (4.25)–(4.27) we obtain equations for the transition temperatures which do not depend on the explicit form of P(E):

$$T_{\rm F} = 2,759cV, \quad T_{\rm C} = 1,966c^{1/2}V.$$
 (4.28)

The critical probabilities of filling c^* and the temperature T^* for the coexistence of three phases are found from the condition $T_F = T_G = T^*$, which yields $c^* = 0.5237$, $T^* = 1.445V$. To calculate the dielectric susceptibility of the system $\chi(T)$ near the PG line of phase transitions one must take into account the next terms of the expansion of $\langle \mathbf{e}_r \rangle_E$ in terms of the field. When these terms are considered the moment $\langle \mathbf{E}^4 \rangle$ appears, which depends on the type of distribution $P(\mathbf{E})$. As a result the temperature dependence $\chi(T)$ is written as follows:⁸¹

$$\begin{split} \chi(T) &= \frac{\mu^2}{2T_G} f(T), \\ f(T) &\approx \begin{cases} [(T/T_G) - \gamma]^{-1}, & T \ge T_G, \\ \{1 - \gamma + [\nu(T_G - T)/T_G]\}^{-1}, & T \le T_G, \end{cases} \end{split}$$
(4.29)

where $\gamma = (c/c^*)^{1/2}$ and the numerical coefficient v depends on the explicit form of $P(\mathbf{E})$, which goes to zero for a twodimensional Gaussian distribution, and is positive if $P(\mathbf{E})$ has a characteristic "trough" at small E(P(0) = 0, Ref. 2). Thus, the slope of $\chi(T)$ at $T < T_G$ near the vertex $T = T_G$ is equal to zero only in theories with a Gaussian distribution of random variables. The dependence of the type of $P(\mathbf{E})$ function on the orientation correlations and the means of preparing the G phase may also affect the form of $\chi(T)$ (which is observed experimentally in spin glasses⁹⁷⁻⁹⁹). The line of coexistence of phases F and G also depends on the form of $P(\mathbf{E})$. In Fig. 10 the dashed line was calculated from Eqs. (4.25)-(4.27) for a two-dimensional Gaussian distribution of random fields. Taking into account the De Almeida-Thouless instability¹⁰⁰ one can confirm that the real FG curve will begin at the same point (T^*,c^*) , but will pass somewhat right of the dashed curve, extending to the point (0.1).

Let us estimate the characteristic dipole energies and phase transition temperatures for a system of OH groups on a SiO₂ surface. At $\mu = 2-2.5$ D and a = 5 Å $V = \mu^2/a^3 = 20-31$ meV, $T_0 - V/k_B = 230-360$ K. If one considers the attenuation of dipole interactions due to the of the substrate static permittivity $\varepsilon_{\rm s} \simeq 3.5$ $V = [2/(1 + \epsilon_s)]\mu^2/a^3 = 9-14 \text{ meV}, T_0 = 100-160 \text{ K}. \text{ At}$ $c \approx 0.5$, $T_F \approx T_G \approx T^* \approx 1.4T_0 = 140-220$ K; however, due to the overestimation by a factor of two of the transition temperatures in the self-consistent field approximation, $T^* \approx 70 - 110$ K. Thus, the lower boundary of the estimates of phase transition temperatures in the system of surface OH groups still substantially exceeds the characteristic transition temperatures $(\sim 1 \text{ K})$ in the dipole glasses which are now being widely studied.² By chemically replacing OH groups with nonpolar radicals one can easily change the concentration parameter c. This yields a system of surface OH groups which are a convenient object for experimental studies of the dipole glass phase. The dielectric susceptibility (Eq. (4.29)) yields a temperature-dependent contribution from the subsystem of surface OH groups to the full permittivity of the sample. A highly dispersed silica may be expediently used for this purpose. Introducing the ratio of the density of silica to the density of quartz ρ/ρ_0 and the ratio for the adsorption lattice constant to the average radius of a globule of silica a/R, we easily obtain an estimate of this contribution:⁸¹ $\Delta \varepsilon(T) \approx 8.6c^{1/2} (\rho/\rho_0) (a/R) f(T)$, which at ρ/ρ_0 and $a/R \sim 0.1$ yields a value which is completely sufficient for an experimental observation $\Delta \varepsilon(T) \sim 0.05 - 0.1$.

Taking $V \sim 10$ meV as the dipole energy per dipole we obtain the following order of magnitude estimate for the contribution of dipole interactions of radicals to surface energy: $\sigma_{dip} \sim V/a^2 \sim 10 \text{ mJ/m}^2$. Characteristic values of the coefficients of surface tension of solids are $\sigma_s \sim 100 \text{ mJ/m}^2$. Thus, the ratio σ_{dip}/σ_s is of the order of 10% and the orientational phase transitions in the system of surface radicals may be fixed using the temperature dependence of the coefficient of surface tension. One way of determining the coefficient of surface tension of a fine film using ultrasonic measurements was proposed in Ref. 101. The dynamics of the motion of polar molecules of a gas in strong surface fields was examined in Refs. 15 and 16. The source of these strong surface fields may be the orientationally ordered phase of surface dipole radicals.

The orientational ordering of surface radicals may also explain the abrupt formation of associates from particles of highly dispersed silica at certain temperatures. As the silica particles approach each other the contribution of dipole interactions between radicals on the surfaces of neighboring particles increases, so the characteristic energy V and transition temperatures may increase severalfold. The orientational mobility of radicals insures the attractive character of dipole forces. Thus, a transition to an orientationally ordered phase at a higher temperature may be the source of the spontaneous appearance of attraction between particles.

5. VIBRATIONAL SPECTRA OF DIPOLE MOLECULES IN VARIOUS ORIENTATIONAL PHASES

Dipole-dipole interaction of extrinsic polar molecules with rotational degrees of freedom has a dual effect on the state of the system. First, orientational phases of dipole moments are formed. These were examined in the preceding section. Second, there is collectivization of the vibrational states of individual molecules, and this depends on the structural arrangement of absorbent molecules on the surface of a solid and on the type of orientational phase. The simplest case which allows classification of the vibrational spectra by a wave vector is realized for lattice structures of molecules with dipole moments ordered by orientation. In the absence of orientational ordering, as well as for random molecular filling of the sites of a lattice of adsorption centers or in the case of topological disorder, the description of the vibrational spectrum of the system encounters characteristic difficulties.¹⁰²⁻¹⁰⁴ These difficulties are further complicated by the need to take into account the anharmonic nature of vibrations that makes a substantial contribution to frequency shifts (of the type of Eqs. (3.19) and (3.21)) under the action of static electric fields of neighboring dipoles, and the inhomogeneous broadening of spectral lines. The analysis of the shape of the spectral lines near the points of orientational phase transitions today still remains an overly complex task.

The first impetus for the analysis of the effect of dipoledipole interactions on the vibrational spectra of absorption molecules was provided by the experiments of Eischens, Francis, and Pliskin,¹⁰⁵ who discovered the dependence of the position of the band of infrared absorption by stretching vibrations of CO molecules on the filling factor of a platinum surface. The equations obtained in Ref. 106 for the frequency shifts of the maxima of the bands in a harmonic approximation assumed the orientational ordering of molecules along the normal to the surface, and a lattice structure of the arrangement of molecules on the surface. Analogous equations which consider the contribution of the electron polarizability of molecules to frequency shifts of the maxima of bands and their intensities were deduced in Refs. 107 and 108 and were discussed in detail in Refs. 19, 29, and 109. The effect of random filling of the sites of an adsorption center lattice with molecules (of the same or different isotopic composition) on the spectrum was studied in Ref. 110 in the framework of a coherent potential approximation. The contribution of orientational disorder in this same approximation was analyzed in Ref. 66.

A very simple model, which takes into account stretching and torsional anharmonic vibrations of an arbitrary system of molecules with dipole interactions with one another and with rotational degrees of freedom, is characterized by the Hamiltonian^{19,111}

$$\begin{aligned} H &= \sum_{j} \left(\frac{p_{xj}^{2}}{2m} + \frac{1}{2}k_{r} x_{j}^{2} - \frac{1}{3}\alpha_{r} x_{j}^{3} \right) + \sum_{j} \left(\frac{p_{\varphi j}^{2}}{2I} + \frac{1}{2}I\omega_{\varphi}^{2}\varphi_{j}^{2} \right) \\ &+ \frac{1}{2}\sum_{j \neq j'} \left(\frac{\delta_{\alpha\beta}}{r_{jj'}^{3}} - 3 \frac{r_{jj'}^{\alpha}r_{jj'}^{\beta}}{r_{jj'}^{5}} \right) \mu_{j}^{\alpha} \mu_{j'}^{\beta} , \end{aligned}$$
(5.1)

where x_j and φ_j are the radial and angular displacements of the j^{th} molecule with reduced mass m, moment of inertia $I = mr_0^2$, force constant k_r , coefficient of cubic anharmonicity α_r , and frequency of isolated torsional vibrations $\omega_{\varphi}; p_{xj}$ and $p_{\varphi j}$ are the corresponding generalized momenta. The dipole moments $\vec{\mu}_j$ can be expanded in terms of small x_j and φ_j in the following manner:

$$\vec{\mu}_{j} \approx \mu \mathbf{e}_{j} + \frac{\partial \vec{\mu}_{j}}{\partial x_{j}} x_{j} \approx \mu \vec{\xi}_{1j} \left(1 - \frac{1}{2}\varphi_{j}^{2}\right) + \mu \vec{\xi}_{2j} \varphi_{j} + q \vec{\xi}_{1j} x_{j}; \quad (5.2)$$

here $q = \mu/r_0$ is the effective charge of the atoms of a molecule with an equilibrium length r_0 and an equilibrium dipole moment μ . The unit vectors $\vec{\xi}_{1j}$ and $\vec{\xi}_{2j}$ give the equilibrium orientation of the radical and the orientation perpendicular to it, along which the torsional vibrations occur. For a lattice system at low temperatures the vectors $\vec{\xi}_{1j}$ and $\vec{\xi}_{2j}$ coincide with the vectors of dipole orientation $\vec{\xi}_1$ (**r**) and $\vec{\xi}_2$ (**r**) in the ground state, and the expansion of \mathbf{e}_j with respect to these unit vectors in Eq. (5.2) is analogous to Eq. (4.12). In the general case, the unit vectors $\vec{\xi}_{1j}$ and $\vec{\xi}_{2j}$, which are perpendicular to each other, may have random orientations corresponding, for each dipole, to *n* equivalent minima of the local potential of hindered rotation (Eq. (3.3)).

After substitution of the expansion in Eq. (5.2) into the initial Hamiltonian in Eq. (5.1), one can isolate two independent Hamiltonians of stretching and torsional vibrations, each of which is written in the same form (which is standard in studies of the spectra of disordered systems¹⁰²):

$$H_{ex} = \hbar \sum_{j} \omega_{j} b_{j}^{+} b_{j} + \frac{\hbar}{4I\omega_{0}} \sum_{j=j'} \xi_{j}^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{j'}^{\beta}(b_{j}^{+} + b_{j})(b_{j'}^{+} + b_{j'}),$$
(5.3)

where $V^{\alpha\beta}(\mathbf{r}_{jj'})$ is the tensor of dipole-dipole interaction introduced in Eq. (4.2a), and b_j^+ and b_j are Bose operators for the creation and annihilation of vibration excitations of the *j*th radical.

For stretching vibrations in a Hamiltonian like Eq. (5.3) (obtained in Ref. 111) we have

$$\begin{split} \xi_{j}^{*} &= \xi_{1j}^{*}, \quad \omega_{0} = \left(\frac{k_{r}}{m}\right)^{1/2} - \frac{5}{6} \frac{\hbar \alpha_{r}^{2}}{mk_{r}^{2}}, \\ \omega_{j}^{2} &= \omega_{0}^{2} + \frac{\varkappa}{I} \sum_{j'(\neq j)} \xi_{1j}^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{1j'}^{\beta}, \quad \varkappa = \frac{2\alpha_{r} r_{0}}{k_{r}}. \end{split}$$
(5.4)

The second term in Eq. (5.3) is responsible for the dynamic renormalization of the frequencies of dipole interaction, while the term which is proportional to \varkappa leads to static renormalization of frequencies, which is due to the effect of the static electric fields of neighboring dipoles (the Stark vibration effect⁷⁴).

Generally speaking, we note that the substrate has different effects on static and dynamic interaction of dipoles. Static interaction has a screening factor like $2/(1 + \varepsilon_s)$ (ε_s is the static permittivity of the substrate), while in dynamic interaction this factor is absent due to the approximate equality $\varepsilon_{\omega} \approx 1$ for high frequencies ω of local vibrations. Nonetheless, to simplify the notations we will not note the presence or absence of this factor in $V^{\alpha\beta}(\mathbf{r}_{jj'})$ and only in estimates for OH groups on a SiO₂ surface will we assume that $V \sim 10$ meV for static interactions and $V \sim 20$ meV for dynamic interactions. The opposite situation, in which static interactions exceed dynamic interactions, is observed in CO groups on a surface of ZnO.^{109,112} This is explained by the increase in the dipole moment of the CO molecule itself in adsorption on ZnO,¹¹³ as well as by an increase in the effective dipole moment of the surface fragment perturbed by the CO group, which is adsorbed along the normal to the surface. In dynamic interactions the substrate atoms are not attracted because the vibrations of the dipole moments occur at frequencies which exceed the phonon frequencies of the substrate.¹⁹

In a ferroelectric state of dipoles ordered by orientation in a triangular lattice, the dispersion law of phonons of stretching vibrations is defined by the equation (see Eqs. (4.3) and (4.4))

$$\omega^{2}(\mathbf{k}) = \omega_{0}^{2} + \frac{1}{I} (\times \widetilde{V}_{1} + \widetilde{V}^{\alpha\beta}(\mathbf{k}) \widetilde{\xi}_{1}^{\alpha}(0) \widetilde{\xi}_{2}^{\beta}(0)), \qquad (5.5)$$

so in the infrared absorption spectrum $(k \rightarrow 0)$ one will observe a band whose frequency will, in the Heitler-London approximation $(|\tilde{V}_1|/I \leqslant \omega_0^2)$, be equal to

$$\omega(0) = \omega_0 + \frac{1}{2I\omega_0} (x+1)\tilde{V}_1.$$
 (5.6)

For OH groups on a SiO₂ surface, based on estimates from Eq. (3.18), we obtain $\varkappa \approx 6.6$ and static renormalization is dominant. Then Eq. (5.6) is actually reduced to Eq. (3.19), in which the electric field $E = -\tilde{V}_1/\mu$ is created by neighboring dipole moments in the ground orientational state. With $\tilde{V}_1 = -5.517V \sim -50$ meV, $\omega_0 \approx 7.07 \cdot 10^{14}$ s⁻¹ (3750 cm⁻¹), $I = 1.48 \cdot 10^{-40}$ g·cm², we obtain from Eq. (5.6) an estimate of the shift in frequency relative to ω_0 : $\omega(0) - \omega_0 \sim -2(\varkappa + 1)$ cm⁻¹ ~ -15 cm⁻¹.

In an orientationally disordered state the spectral characteristics of the system in the Heitler–London approximation are defined by the following Green's function:^{66,111,114}

$$G_{jj'}^{\alpha\beta}(t) = -i\theta(t)\xi_j^{\alpha}(t)\xi_{j'}^{\beta}(0)\langle [b_j(t), b_{j'}^+(0)] \rangle_{\text{ex}}, \qquad (5.7)$$

which should be averaged over all possible orientations of the unit vectors $\vec{\xi}_j$. If the spatial structure of radicals is to be characterized by the probability c of filling the sites of a lattice of adsorption centers, the orientation averaging must be supplemented by averaging over all possible configurations of radicals in the lattice. Then the desired spectral function and the distribution function of frequencies will be equal to

$$S(\omega) = -\frac{1}{\pi N} \text{Im} \sum_{j,j'} \langle G_{jj'}^{aa}(\omega) \rangle,$$

$$\rho(\omega) = -\frac{1}{\pi N} \text{Im} \sum_{j} \langle G_{jj}^{aa}(\omega) \rangle,$$
(5.8)

where $G_{jj'}^{\alpha\beta}(\omega)$ is the frequency Fourier component of $G_{jj'}^{\alpha\beta}(t)$, which for small average reorientational frequencies w_j (see Eq. (3.15)) compared to the vibration frequencies ω_j , satisfies the equation

$$\begin{split} G_{jj'}^{\alpha\beta}(\omega) &= g_{j}^{\alpha\beta}(\omega)\delta_{jj'} + \frac{1}{2I\omega_{0}}g_{j}^{\alpha\nu_{1}}(\omega)\sum_{j''}V^{\nu_{1}\nu_{2}}(\mathbf{r}_{jj''})G_{j''j}^{\nu\beta}(\omega), \\ g_{j}^{\alpha\beta}(\omega) &= \xi_{j}^{\alpha}\xi_{j}^{\beta}g_{j}(\omega), \quad g_{j}(\omega) = (\omega - \omega_{j} + iw_{j})^{-1}. \end{split}$$

$$\end{split}$$

$$(5.9)$$

The moments of the spectral function and the distribution function of frequencies

$$M_{sp} = \int_{-\infty}^{\infty} (\omega - \omega_0)^p S(\omega) d\omega, \quad M_{\rho p} = \int_{-\infty}^{\infty} (\omega - \omega_0)^p \rho(\omega) d\omega$$
(5.10)

is defined at $w_i \rightarrow +0$ by the equations¹¹¹

$$M_{sp} = N^{-1} \langle \sum_{jj'} \xi_j^{\alpha} (\widehat{A}^{\rho})_{jj'} \xi_{j'}^{\alpha} \rangle, \quad M_{\rho p} = N^{-1} \langle \sum_{j} (\widehat{A}^{\rho})_{jj} \rangle,$$

$$A_{jj'} = \frac{1}{2I\omega_0} \left(\xi_j^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{j'}^{\beta} + \varkappa \delta_{jj'} \xi_{1j}^{\alpha} \sum_{j'' (\boldsymbol{*}_j)} V^{\alpha\beta}(\mathbf{r}_{jj''}) \xi_{1j''}^{\beta} \right).$$
(5.11)

If the unit vectors $\dot{\xi}_j$ have arbitrary two-dimensional orientations and there is no correlation of $\vec{\xi}_j$ in the neighboring radicals:

$$\langle \xi_{j}^{*} \rangle = 0, \quad \langle \xi_{j}^{\alpha} \xi_{j'}^{\beta} \rangle = \frac{1}{2} \delta_{jj'} \delta_{\alpha\beta}, \tag{5.12}$$

then for a triangular lattice of adsorption centers the moments of the spectral function will be equal to the following expressions:¹¹¹

$$\omega_1 \equiv \omega_0 + M_{S1} = \omega_0 + \frac{1}{4I\omega_0}c\tilde{V}_1 = \omega_0 - 2,759c\lambda,$$

$$\hat{M}_{S2} = \overline{(\omega - \omega_1)^2} = 3,985c\lambda^2(x^2c + 2 - c), \quad \lambda \equiv V/2I\omega_0,$$

$$\hat{M}_{S3} = \overline{(\omega - \omega_1)^3}$$
(5.13)

$$= 16,0c\lambda^3[1,829\times^2(c-0,559) + (1,944-c)(c-0,176)].$$

The shift of the "center of gravity" of the spectral function relative to ω_0 is a small negative value and is associated exclusively with the dynamic interaction of dipole moments (because there is no parameter κ). At c = 1, M_{S1} in Eq. (5.13), due to orientational disorder, is a factor of two smaller than in Eq. (5.6) at $\kappa = 0$, and is ~ -1 cm⁻¹. Due to the presence of orientational disorder the RMS width $S(\omega)$ rises monotonically as the parameter c increases and is nonzero even for maximum filling of adsorption centers (c = 1). The asymmetry of the spectral function at $\kappa^2 \ge 1$ is positive (negative) when c > 0.56 (c < 0.56). When $\kappa = 0$, Eq. (5.13) switches to the equations obtained in Refs. 66 and 114.

The spectral function of a disordered system of anharmonic oscillators with $x^2 \ge 1$ and $w_j = w$ is approximately described by an asymmetrical Gaussian function:¹¹¹

$$S(\omega) \approx -\pi^{-1} \operatorname{Im}(2\pi \hat{M}_{S2})^{-1/2} \times \int_{-\infty}^{\infty} \frac{1 - \{\hat{M}_{S3}x[1 - (x^2/3)]/2\hat{M}_{S2}^{3/2}\}}{x_{\omega} - x + iw} e^{-(1/2)x^2} dx,$$

$$x_{\omega} = \hat{M}_{S2}^{-1/2} (\omega - \omega_0 - M_{S1}), \qquad (5.14)$$

which depends on the exact values of the moments in Eq. (5.13). Figure 11 shows the frequency dependences $S(\omega)$ as $\omega \to +0$ for various values of c. Equation (5.14) makes it possible to link the half-width $\Delta \omega_{1/2}$ at the half-height of the distribution $S(\omega)$ with the second moment \hat{M}_{S2} : as $\omega \to 0$, $\Delta \omega_{1/2} = (2\hat{M}_{S2} \ln 2)^{1/2} \approx 2(2 \ln 2)^{1/2} \times c\lambda \sim 6c \text{ cm}^{-1}$. The resultant estimate at $c \sim 0.3$ agrees with the value $\Delta \omega_{1/2} \approx 2 \text{ cm}^{-1}$, which was experimentally obtained in Ref. 9 for T < 400 K (see the discussion of Eq. (2.2)). The value of $c \sim 0.3 < 0.56$ and the asymmetry of the spectral function is negative (see Fig. 11), which is also observed when the temperature at which the spectra are taken is dropped.

Here it should be noted that the negative asymmetry of the spectral function may also result from OH groups located near the junctions of globules of highly dispersed silica,



FIG. 11. Frequency dependences of the spectral function S of an orientationally disordered two-dimensional system of anharmonic oscillators at c = 0.3 (1), 0.7 (2), and 1 (3).

because the frequency of their stretching vibrations, according to Eq. (3.19), should be lower due to the perturbing electric fields of OH groups in the neighboring globule.⁷³ Estimates show that for a globule of radius ~ 50 Å the number of such perturbed groups in relation to the total number is $\sim 1-2\%$.

For a system of arbitrarily oriented harmonic oscillators $g_j(\omega) = g(\omega)$, and the Green's function $g_j^{\alpha\beta}(\omega)$ in Eq. (5.9) becomes a locator function, because it does not depend on interaction with other oscillators. Due to the equality $\omega_j = \omega_0$ the Hamiltonian in Eq. (5.3) contains only nondiagonal disorder of the multiplicative structure $\xi_j^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{j'}^{\beta}$, which, in contrast to Ref. 115, arises from the problem statement itself (and not as a means of an approximate description) and is defined by the random unit vectors ξ_j . This makes it possible when $1 - c \ll 1$ to use the coherent potential approximation, which leads to the following results:⁶⁶

$$\langle \hat{G}_{c_{\text{pa}}}(\mathbf{k},\omega) \rangle = \left(\hat{\sigma}^{-1}(\omega) - \frac{1}{2I\omega_0} \tilde{V}(\mathbf{k}) \right)^{-1},$$
 (5.15)

where the locator of the effective medium $\sigma^{\alpha\beta}(\omega)$ is the root of the matrix equation

$$\hat{G}_{0} = \langle \hat{g} [\hat{1} - (\hat{\sigma}^{-1} - \hat{G}_{0}^{-1})\hat{g}]^{-1} \rangle,$$

$$\hat{G}_{0}(\omega) = N_{0}^{-1} \sum_{\mathbf{k}} \langle \hat{G}_{cpa} \quad (\mathbf{k}, \omega) \rangle$$
(5.16)

(N_0 is the number of lattice sites in the main area). For equally probable orientations of $\vec{\xi}_j$ in a *d*-dimensional space and an isotropic effective medium filling a space of the same dimension *d*, the equation for σ is simplified:

$$\sigma^{-1} = g^{-1} + [1 - (c/d)]G_0^{-1}.$$
(5.17)

The spectral function and the distribution function of frequencies, in the framework of the coherent potential approximation,

$$S(\omega) = -(\pi c)^{-1} \operatorname{Im} \langle \widehat{G}_{cpa}^{\alpha \alpha} (\mathbf{k} = 0, \omega) \rangle, \qquad (5.18)$$



FIG. 12. Frequency dependences of the spectral function S and density of states ρ of an orientationally disordered system of harmonic oscillators in a triangular lattice in the coherent potential approximation $(\tilde{\lambda} = |\tilde{V}_1|/2I\omega_0 = 5.517\lambda)$.

$$\rho(\omega) = -(\pi c N_0)^{-1} \operatorname{Im} \sum_{\mathbf{k}} \langle \hat{G}_{cpa}^{\alpha\alpha} (\mathbf{k}, \omega) \rangle$$

were calculated for a triangular dipole lattice (c = 1) in Ref. 66 on the basis of an analytical approximation (Eq. (4.9)), and are presented in Fig. 12. Analogous calculations in the framework of the coherent potential approximation for a simpler system of CO groups with orientational ordering by dipole moments perpendicular to the plane of the surface were done in Ref. 110 for various values of c. However, as shown in Refs. 111 and 114, the accuracy of such calculations is substantially reduced as \varkappa increases and as c decreases, and at $c < (\varkappa + 1)/(2\varkappa + 8.31)$ one obtains in the framework of the coherent potential approximation even an incorrect sign for the asymmetry of the spectral function.

Let us now turn to a description of the spectrum of torsional vibrations. The Hamiltonian for torsional vibrations is given by Eq. (5.3) with

$$\boldsymbol{\xi}_{j}^{*} = \boldsymbol{\xi}_{2j}^{*}, \quad \boldsymbol{\omega}_{0} = \boldsymbol{\omega}_{\varphi}, \quad \boldsymbol{\omega}_{j}^{2} = \boldsymbol{\omega}_{\varphi}^{2} - \frac{1}{I} \sum_{j' (\neq I)} \boldsymbol{\xi}_{1j}^{\alpha} \boldsymbol{V}^{\alpha\beta}(\mathbf{r}_{jj'}) \boldsymbol{\xi}_{1j'}^{\beta}.$$
(5.19)

In contrast to Eq. (5.4), the dynamic renormalization of frequencies is defined by the unit vectors $\vec{\xi}_{2j}$, while the static renormalization, Eq. (5.19), again contains unit vectors $\vec{\xi}_{1j}$ (thus, one can establish the following formal correspondence of parameters between Eqs. (5.19) and (5.4): $\omega_0 = \omega_{\varphi}, \, \varkappa = -1$). Moreover, now $|\tilde{V}_1|/I \sim \omega_{\varphi}^2$, and the Heitler-London approximation is inapplicable. Bearing this in mind, one can easily switch from the results of Eqs. (5.5)-(5.18) for stretching vibrations to analogous equations for torsional vibrations. The orientational vibrations of arbitrary two-dimensional dipole lattices (with $\omega_{\varphi} = 0$) were examined in Refs. 38 and 88. We present here only two exact equations for the first moments of the squares of the frequencies of the spectral function and the density of states (the distribution function of the squares of the frequencies):

$$\begin{split} \langle \omega^2 \rangle_S \\ &= \omega_{\varphi}^2 - \frac{1}{NI} \sum_{j \neq j'} \xi_{1j}^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{1j'}^{\beta} + \frac{1}{NI} \sum_{j \neq j'} \xi_{2j}^{\gamma} \xi_{2j}^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{2j'}^{\beta} \xi_{2j'}^{\gamma}, \\ \langle \omega^2 \rangle_{\rho} &= \omega_{\varphi}^2 - \frac{1}{NI} \sum_{j \neq j'} \xi_{1j}^{\alpha} V^{\alpha\beta}(\mathbf{r}_{jj'}) \xi_{1j'}^{\beta}, \end{split}$$
(5.20)

which have not been averaged over the spatial and orientational disorders, and thus, depend on the arbitrary orientations of unit vectors $\vec{\xi}_{1j}$ and $\vec{\xi}_{2j}$, which are perpendicular to each other. We recall that, according to Eqs. (3.9) and (3.10), the spectral function of torsional vibrations describes the spectral lines of infrared absorption in the longwavelength region $\sim 200 \text{ cm}^{-1}$, while the density of states of torsional vibrations approximately describes the spectral lines of the composite frequencies $\omega \sim \omega_r \pm \omega_{\varphi}$ due to the "opening" of a wide band of torsional vibrations on the background of a narrow band of stretching vibrations in transitions with simultaneous change in two quantum numbers¹⁹:

$$S_{rp}(\omega^2) \propto \left[\frac{\theta(\omega-\omega_r)}{1-e^{-\hbar(\omega-\omega_r)/T}} + \frac{\theta(\omega_r-\omega)}{e^{\hbar(\omega_r-\omega)/T}-1}\right] \rho((\omega-\omega_r)^2).$$
(5.21)

Thus, Eqs. (5.20) and (5.21) make it possible to analyze the spectral behavior of torsional vibrations in various orientational phases.

For a high-temperature paraelectric orientational phase or for an orientationally disordered phase of dipole glass, the unit vectors in Eq. (5.20) should be averaged using Eq. (5.12), which for a triangular lattice of adsorption centers filled by radicals with probability c, yields

$$\langle \omega^2 \rangle_S = \omega_{\varphi}^2 + \frac{1}{2I} c \widetilde{V}_1, \quad \langle \omega^2 \rangle_{\rho} = \omega_{\varphi}^2. \tag{5.22}$$

In the case of a ferroelectric orientationally ordered state of dipoles in a triangular lattice (c = 1) from Eq. (5.20) we obtain

$$\omega_{S}^{2} = \omega_{\varphi}^{2}, \quad \langle \omega^{2} \rangle_{\rho} = \omega_{\varphi}^{2} - \frac{1}{I} \widetilde{V}_{1}. \tag{5.23}$$

Since $\tilde{V}_1 < 0$, ferroelectric ordering leads to an increase in the effective frequencies of torsional vibrations by a quantity of the order of $|\tilde{V}_1|/(2I\omega_{\varphi}) \simeq 40 \text{ cm}^{-1}$ (for $I = 1.48 \cdot 10^{-40}$ $\text{g} \cdot \text{cm}^2$, $\omega_{\varphi} = 200 \text{ cm}^{-1}$ and energy of static interactions $\tilde{V}_1 = -50 \text{ meV}$) in accordance with the result of Eq. (3.21) of the simplified examination. In section 2 we recalled the result of Ref. 12 on the increase in the frequency of the observed band $\omega_r + \omega_{\varphi} \simeq 3850 \text{ cm}^{-1}$ by 30 cm⁻¹ when the sample was cooled with liquid helium, which agrees with the estimates which were presented, that took into account the orientational ordering of dipoles.

Equation (5.22) (and Eq. (5.23) for $\langle \omega^2 \rangle_{\rho}$) are not well suited for direct quantitative estimates of the frequencies of the maxima of spectral lines, because the latter and the corresponding "centers of gravity" of the frequency distributions may substantially differ (see, for example, Fig. 12). Thus, for these estimates we use the results of numerical calculations for a triangular dipole lattice (c = 1) in the framework of the coherent potential approximation. The frequencies of the maxima of functions $S(\omega)$ and $\rho(\omega)$ in Fig. 12, which are defined by the dynamic interactions of dipole moments with $\tilde{V}_1 \simeq -100$ meV, are approximately equal to

$$\omega_{\max}^{(S)} \approx (\omega_{\varphi}^{2} - 0.80 | \tilde{V}_{1} | I^{-1})^{1/2} \approx 120 \text{ cm}^{-1},$$

$$\omega_{\max}^{(\rho)} \approx (\omega_{\varphi}^{2} - 0.64 | \tilde{V}_{1} | I^{-1})^{1/2} \approx 140 \text{ cm}^{-1}.$$
(5.24)

Thus, the experimental value $\omega_{\max}^{(\rho)} \sim 100 \text{ cm}^{-1}$ (in Refs. 10– 12 wide bands were observed at 3650 and 3850 cm⁻¹ which were about 100 cm⁻¹ away from the narrow band at 3750 cm⁻¹), and a distinct peak with $\omega_{\max}^{(S)} \simeq 104 \text{ cm}^{-1}$ in Fig. 2 can be matched with the value $\omega_{\varphi} \simeq 200 \text{ cm}^{-1}$ for isolated torsional vibrations when one takes into account dipole-dipole interactions.⁶⁶ Since the quantities ω_{φ}^2 and *I* are proportional to m^{-1} , then $\omega_{\max}^{(S,\rho)} \sim m^{-1/2}$ and in $H \leftrightarrow D$ -exchange, an observed decrease in $\omega_{\max}^{(\rho)}$ by a factor of about $\sqrt{2}$ occurs.

6. CONCLUSION

The basic approaches in solid state theory correspond to the following two levels of description: 1) calculations of the electron band structure, of the force constants, and of other characteristics of crystals from first principles (using only fundamental physical constants, data on the electron structure of atoms and basic equations of quantum mechanics); 2) statistical description of observed macroscopic quantities (electron and vibrational spectra of crystals) in terms of collective variables (excitons, phonons, and other quasiparticles) and using the values of the crystal characteristics calculated from first principles or estimated from experimental data. At present, this type of classification may also be used in the theory of vibrational spectra of surface groups of atoms. Quantum chemical calculations of the electron structure and force constants of surface formations yield information from first principles, for example, on the vibration frequencies of some isolated groups of atoms on various substrates. In this survey we discuss results obtained in the framework of the second level of description, which operates on given values of characteristics of individual groups of atoms and explains effects considering the macroscopically large number of degrees of freedom of substrate atoms and the interaction of surface groups of atoms. This consideration is especially important for low-energy orientational states, because the transitions between them are resonantly coupled with the phonon spectrum of the substrate; reorientation is characterized by a temperature dependence which cannot be calculated without a statistical description.

For a sufficiently complete interpretation of observed spectra of surface groups of atoms one must use the approaches of the two levels of description. Nonetheless, at present first-level interpretation predominates, and it seems self-sufficient because the majority of experimental data is only for one temperature point, room temperature. For example, in the spectroscopy of OH groups on an Al₂O₃ surface it would make sense to analyze the temperature dependence of each of the observed spectral lines, which would make it possible to link them with OH groups on various surface centers (independent of the temperature intensity of lines) or with the vibrational-orientational transitions (temperature-dependent broadening and intensity). On the other hand, it would be unjustified to use the results of only the second level of description to interpret the experimental spectra of identical surface centers, although this is tempting, because sets of spectral lines are frequently described by vibrational-orientational transitions of one center, and do not require additional assumptions about their differences. Thus, from a practical point of view, the further development of the theory should unite both levels of description, which would be more awkward, but more suited to the nature of the objects under study.

The study of the orientational states of interacting dipole groups of atoms with rotational degrees of freedom led to the statement of a number of fundamental problems which are of general theoretical interest: the description of thermoactive reorientations and tunnel relaxation of orientational states of extrinsic radicals in the phonon field of the framework or substrate, the possibility of establishing the orientational long-range order in a two-dimensional lattice system with dipole-dipole interaction and a description of the orientational phase transitions, the analysis of orientational states and the spectrum of vibrations of a system of dipoles with a disordered surface arrangement. Some of these problems have already been solved, and this is reflected in this survey. The most detailed exposition of the described issues can be found in Ref. 19 and in recent articles.^{34–38,88–90}

Nonetheless, there still are a number of fundamental problems which must be solved. They include the description of the average characteristics of the two-dimensional phase of dipole glass with an exact consideration of anisotropic dipole-dipole interactions, thermodynamic characteristics of orientational phase transitions in two-dimensional dipole lattices, analysis of the vibrational spectra near the points of phase transitions, and relaxation phenomena in spectra in the dipole glass phase.

The prospects for further experimental studies of these systems consist of measurements of spectroscopic characteristics of surface OH(D) groups (or similar objects) in a wide range of temperatures (including extremely low temperatures) in the long-wavelength infrared region (~ 100 cm⁻¹), as well as the area of composite frequencies at 3750 cm⁻¹. Estimates show that the volume concentration of surface OH groups of highly dispersed matter is completely sufficient to determine the temperature anomalies of heat capacity and permittivity due to orientational phase transitions.

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