Lateral interactions of adsorbed molecules

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Methods for calculating the lateral interactions in systems of adsorbed molecules are discussed. These methods make it possible to find the stable orientational structures of polar molecules as well as the characteristics of the vibrational and electronic spectra of the adsorbate. Several new results concerning the determination of the ground state of dipoles on a flat hexagonal lattice (of the honeycomb type) are presented. It is shown that dipoles in this state form a complicated antiferroelectric vortex structure. When the dipoles are tilted with respect to the plane of the lattice, the tilting being associated with the action of adsorption potentials, such a structure is characterized by Davydov splitting of the spectral lines in two perpendicular polarizations. © *1995 American Institute of Physics.*

The need to understand the mechanisms leading to the formation of complicated orientational structures of adsorbed molecules and to describe the orientational, vibrational, and electronic excitations in these systems has led to the development of a new scientific direction in the surface physics of solids—the theoretical study of the properties of two-dimensional dipole systems. Dipole-dipole interactions make the main contribution to the lateral interactions of the dynamic dipole moments of the vibrational and electronic excitations of adsorbed molecules, as well as to the lateral interactions of the static dipole moments of polar molecules. In many cases, the adsorbed molecules can assume several equivalent orientations in the plane of the lattice of adsorption centers. Then the dipole-dipole interactions of the static dipole moments can form orientationally ordered structures, which arise by means of an orientational phase transition at definite low temperatures.[1–5] The existence of such transitions was proved experimentally for the system CO/NaCl (100),[6] in which low-temperature Davydov splitting of the spectral lines of the valence vibrations of CO molecules was observed.

As a result of the anisotropy of the dipole forces, the dipole moments in the ground state have complicated configurations, which have been calculated, taking into account the long-range action, by different methods for square,[3,7] triangular,[3] orthorhombic,[8] and arbitrary planar Bravais lattices.[9] In the present paper we shall show, for the example of the calculation of the orientational structures and characteristics of the spectra of systems with several nonequivalent molecules in the unit cell of a two-dimensional lattice, that all information about the lateral interactions of the system at hand is contained in the Fourier components of the dipole-dipole interaction tensors. Lattice-sublattice relations, which make it possible, specifically, to express the energy of different orientational structures on a complicated hexagonal lattice in terms of known quantities for triangular sublattices, will be obtained for these quantities. In the process, the ground state of the system under discussion, the dispersion laws of the collective excitations, and the frequencies of the valence vibrations of dipoles which are active in the infrared absorption spectra will be determined.

We consider an arbitrary planar lattice of adsorbed molecules, which is formed by the local crystal field of the surface. We assume that the lattice is a compound lattice and consists of n Bravais sublattices with the unit cell $\mathbf{A}_1,\mathbf{A}_2$. Then its sites can be described by the vectors $\mathbf{R}+\mathbf{r}_j$, where $\mathbf{R}=m_1\mathbf{A}_1+m_2\mathbf{A}_2$ are the sites of the basic Bravais sublattice (m_1 and m_2 are integers) and $\mathbf{r}_j$ is the position of a site in the jth sublattice in the unit cell $(\mathbf{A}_1,\mathbf{A}_2)$. The adsorbed molecules are characterized by the dipole moments $\boldsymbol{\mu}_{\mathbf{R}j}$, whose interactions we intend to take into account here. Since our objective in the present paper is to analyze the lateral interactions, the effects associated with the action of the substrate (which were discussed in detail in, for example, Refs. 4 and 5) will be assumed to have been taken into account and incorporated in the parameters of the adsorbed molecules. We shall show how and when such an analysis is justified.

First, the local crystal fields are already taken into account by the fact that a lattice of adsorption centers has been formed and the high adsorption energies make it possible to ignore effects which are due to desorption of molecules. The orientationally dependent part of the potential energy of a molecule in the crystal field of the substrate in many cases gives rise to several symmetrically equivalent minima, separated by energy barriers which are much less than the adsorption energies and are of the order of the room-temperature thermal energies or lateral-interaction energies.[4,5] The curvature of these minima determines the frequency ω_φ of torsional vibrations of an individual adsorbed molecule and is found to be on the order of 100 cm^{-1}. As a result of the interaction with low-frequency phonons of the substrate, a torsional vibration becomes resonant. For this reason, the renormalized frequency $\tilde{\omega}_\varphi$ (which is virtually identical to ω_φ) and the width of the resonant vibration can be treated as parameters of the adsorbed molecule. These parameters, within the exchange dephasing model, which takes into account the finiteness of the reorientation barrier,[10] determine the frequency ω_{0j} and damping Γ_j of high-frequency local molecular vibrations associated with the longitudinal displacement $x_{\mathbf{R}j}$ of the dipole-moment vector: $\boldsymbol{\mu}_{\mathbf{R}j} = (\mu_j + q_j x_{\mathbf{R}j})\mathbf{e}_{\mathbf{R}j}$ (q_j is the effective charge and $\mathbf{e}_{\mathbf{R}j}$ is the unit vector of the orientation of the static dipole moment μ_j).

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In experiments the spectral lines of high-frequency longitudinal vibrations of adsorbed molecules, such that the frequencies $\omega_{0j} > 2000\ \mathrm{cm}^{-1}$ are much higher than the vibrational frequencies of the substrate atoms, are easily recorded. The damping Γ_j of these vibrations is less than $1\ \mathrm{cm}^{-1}$ at low temperatures (see, for example, Ref. 6) and is found to be an order of magnitude less than the width of the band formed by the lateral interactions. For this reason, if only the observed frequency of the spectral line of a collective excitation is of interest, then $\Gamma_j = 0$. In this case, the longitudinal vibration is split off from the transverse orientational vibration because their polarizations are orthogonal to one another and the values of the corresponding frequencies differ by an order of magnitude.

Orientational ordering of polar molecules on simple planar lattices, taking into account the local hindered-rotation potentials, was studied in Ref. 3. As a result of one-parameter degeneracy (in the absence of the crystal field) of the ground states of the dipoles on square and triangular lattices, the local potentials could easily deform the orientational structure without changing the dipole-interaction energy. For this reason, in the present paper, in analyzing the ground state of the orientational part of the Hamiltonian of the interacting static dipole moments on a compound lattice, we shall not explicitly study the orientationally dependent part of the potential energy of the molecule in the substrate crystal field, and in the subsequent problems of describing the vibrational spectra of the high-frequency longitudinal vibrations, the existence of such a crystal field will be manifested in the choice of a definite orientational structure $\mathbf{e}_{\mathbf{R}j}$.

The forgoing discussion of the model of lateral interactions of adsorbed molecules therefore enables us to represent the complete Hamiltonian of the system at hand as the sum

$$H = H_0 + H_{\mathrm{ex}}, \tag{1}$$

consisting of static dipole-dipole interactions

$$\begin{aligned} H_0 &= \frac{1}{2} \sum_{\mathbf{R}j,\mathbf{R}'j'} \mu_j \mu_{j'} V^{\alpha\beta}(\mathbf{R}-\mathbf{R}'+\mathbf{r}_{jj'}) e^{\alpha}_{\mathbf{R}j} e^{\beta}_{\mathbf{R}'j'} \\ &= \frac{1}{2} N_0 \sum_{\mathbf{K}jj'} \mu_j \mu_{j'} \tilde{V}^{\alpha\beta}_{jj'}(\mathbf{K}) \tilde{e}^{\alpha}_j(-\mathbf{K}) \tilde{e}^{\beta}_{j'}(\mathbf{K}) \end{aligned} \tag{2}$$

and the Hamiltonian of longitudinal vibrational excitations

$$\begin{aligned} H_{\mathrm{ex}} &= \sum_{\mathbf{R}j} \left(\frac{P^2_{\mathbf{R}j}}{2m_j} + \frac{1}{2} m_j \omega^2_{\mathbf{R}j} x^2_{\mathbf{R}j} \right) \\ &+ \frac{1}{2} \sum_{\mathbf{R}j,\mathbf{R}'j'} q_j q_{j'} e^{\alpha}_{\mathbf{R}j} V^{\alpha\beta}(\mathbf{R}-\mathbf{R}' \\ &+ \mathbf{r}_{jj'}) e^{\beta}_{\mathbf{R}'j'} x_{\mathbf{R}j} x_{\mathbf{R}'j'}. \end{aligned} \tag{3}$$

Here,

$$V^{\alpha\beta}(\mathbf{R}) = \frac{\delta_{\alpha\beta}}{R^3} - 3\,\frac{R_\alpha R_\beta}{R^5} \tag{4}$$

is the dipole-dipole interaction tensor, the second term in Eq. (2) corresponds to a transition to Fourier components within the main region of the basal Bravais sublattice consisting of N_0 sites, $p_{\mathbf{R}j} = m_j \dot{x}_{\mathbf{R}j}$ is the momentum corresponding to the vibration $x_{\mathbf{R}j}$ with reduced mass m_j, and summation over the repeated Greek indices of the Cartesian coordinate axes is implied. The frequency $\omega_{\mathbf{R}j}$ depends on the static electric fields generated by neighboring dipoles. When the cubic anharmonicity α_j of the vibrations of an isolated jth molecule, characterized by the force constant k_j and frequency

$$\omega_{0j} = \left(\frac{k_j}{m_j} \right)^{1/2} - \frac{5}{6}\,\frac{\hbar \alpha_j^2}{m_j k_j^2}, \tag{5}$$

is taken into account, the static renormalization of the frequency can be written as follows:[4,5]

$$\omega^2_{\mathbf{R}_j} = \omega^2_{0j} + \frac{2\alpha_j q_j}{m_j k_j} \sum_{\mathbf{R}'j'} \mu_{j'} e^{\alpha}_{\mathbf{R}j} V^{\alpha\beta}(\mathbf{R}-\mathbf{R}'+\mathbf{r}_{jj'}) e^{\beta}_{\mathbf{R}'j'}. \tag{6}$$

We now consider two basic problems which arise for the system under discussion. The first problem is to determine the ground state of a system of static dipole moments on a lattice and is equivalent to minimizing H_0 over all possible orientations of the vectors $\mathbf{e}_{\mathbf{R}j}$. In so doing, we assume that all molecules are identical ($\mu_j = \mu$), and the orientations $\mathbf{e}_{\mathbf{R}j}$ can be arbitrary in the absence of dipole-dipole interactions. The eigenvalues and eigenvectors of the tensor

$$\begin{gathered} \sum_{j'} \tilde{V}^{\alpha\beta}_{jj'}(\mathbf{K}) C^{\beta\nu}_{j'p}(\mathbf{K}) = V^{\nu}_p(\mathbf{K}) C^{\alpha\nu}_{jp}(\mathbf{K}), \\ (j,p = 1,\dots,n, \quad \nu = 1,2,3) \end{gathered} \tag{7}$$

make it possible to represent the quadratic form (2) as a sum of squares

$$H_0 = \frac{1}{2} N \mu^2 \sum_{\mathbf{K},p,\nu} V^{\nu}_p(\mathbf{K}) |\eta^{\nu}_p(\mathbf{K})|^2,$$

$$N = n_0 N_0, \quad \sum_{\mathbf{K},p,\nu} |\eta^{\nu}_p(\mathbf{K})|^2 = 1, \tag{8}$$

$$e^{\alpha}_{\mathbf{R}j} = n^{1/2} \sum_{\mathbf{K},p,\nu} C^{\alpha\nu}_{jp}(\mathbf{K}) \eta^{\nu}_p(\mathbf{K}) \exp[i\mathbf{K}(\mathbf{R}+\mathbf{r}_j)]. \tag{9}$$

Now, it is obvious that the ground-state energy of the system is determined by the deepest minimum of the family of functions $V^{\nu}_p(\mathbf{K})$, and the corresponding configuration of dipole moments $\mathbf{e}_{\mathbf{R}j}$, as follows from the relation (9), is determined by the eigenvectors $C^{\alpha\nu}_{jp}(\mathbf{K})$. The procedure, presented here, of seeking the ground state of a system of dipoles on a compound lattice is an extension of the analogous procedure for simple Bravais lattices.[9]

The second problem is to find the frequencies of the normal vibrations and the corresponding integral intensities of spectral lines active in the IR-absorption spectra. To solve this problem, the orientations $\mathbf{e}_{\mathbf{R}j}$ of the molecules may be regarded as given. Here, it is unimportant whether or not the orientational structure $\mathbf{e}_{\mathbf{R}j}$ was determined as a result of minimizing the energy of static dipole-dipole interactions or as a result of competition between other interactions (for example, adsorption potentials and Coulomb interactions). In the case of nonpolar molecules ($\mu_j=0$) the vectors $\mathbf{e}_{\mathbf{R}j}$ will describe the orientation of the dynamic transition-dipole moments.

We shall be interested in the periodic orientations of the dynamic dipole moments, when it can be assumed that a unit cell of a two-dimensional crystal contains n orientationally nonequivalent molecules, i.e.,

$$\mathbf{e}_{\mathbf{R}j}=\mathbf{e}_j, \quad \omega_{\mathbf{R}j}^2=\omega_j^2, \quad j=1,\ldots,n. \tag{10}$$

We call attention to an important circumstance which arises in the second problem. The periods of the orientational structure (9) can exceed the periods $\mathbf{A}_1$ and $\mathbf{A}_2$ of the basal Bravais sublattice. In this case, the unit cell $\mathbf{A}_1,\mathbf{A}_2$ must be enlarged so that the conditions (10) would be satisfied and translations by the new vectors $\mathbf{R}$ would reproduce the orientations of the adsorbed molecules.

Now in the excitation Hamiltonian (3) we can go over to the Fourier representation in the wave vector $\mathbf{K}$:

$$H_{\text{ex}}=\sum_{\mathbf{K}} H_{\text{ex}}(\mathbf{K}), \quad H_{\text{ex}}(\mathbf{K})=\sum_j \left(\frac{|\tilde{p}_{\mathbf{K}j}|^2}{2m_j} + \frac{1}{2} m_j\omega_j^2\left|\tilde{x}_{\mathbf{K}j}\right|^2\right) + \frac{1}{2}\sum_{jj'} q_jq_{j'}e_j^\alpha \tilde{V}_{jj'}^{\alpha\beta}(\mathbf{K})e_{j'}^\beta \tilde{x}_{\mathbf{K}j}\tilde{x}_{-\mathbf{K},j'} \tag{11}$$

and we can introduce the normal coordinates ξ_l for the mode $\mathbf{K}=0$ of interest to us, which is seen in infrared spectra:

$$\tilde{x}_{0j}=m_j^{-1/2}\sum_l S_{jl}\xi_l, \quad \tilde{p}_{0j}=m_j^{1/2}\sum_l S_{jl}\dot{\xi}_l. \tag{12}$$

Here the unitary matrices S_{jl}

$$\sum_j S_{jl}S_{jl'}^*=\delta_{ll'}, \quad \sum_l S_{jl}S_{j'l}^*=\delta_{jj'} \tag{13}$$

are constructed from the eigenvectors of the following matrix of squared frequencies:

$$\Phi_{jj'}=\omega_j^2\delta_{jj'}+\frac{q_jq_{j'}}{\sqrt{m_jm_{j'}}} e_j^\alpha \tilde{V}_{jj'}^{\alpha\beta}(0)e_{j'}^\beta, \tag{14}$$

$$\omega_j^2=\omega_{0j}^2+\frac{2\alpha_jq_j}{m_jk_j} e_j^\alpha \sum_{j'} \tilde{V}_{jj'}^{\alpha\beta}(0)e_{j'}^\beta\mu_{j'}. \tag{15}$$

The eigenvalues Ω_l^2 of the same matrix, which satisfy the equation

$$\sum_{j'} \Phi_{jj'}S_{j'l}=\Omega_l^2S_{jl}, \tag{16}$$

determine the squared frequencies of the normal vibrations:

$$H_{\text{ex}}(0)=\frac{1}{2}\sum_l (|\dot{\xi}_l|^2+\Omega_l^2|\xi_l|^2). \tag{17}$$

The IR absorption coefficient $A(\omega)$ of a monolayer of adsorbed molecules with surface concentration N/F is determined by the angle of incidence ϑ of the radiation with respect to the normal to the surface and the effective absorption cross section $\sigma(\omega)$ as follows:

$$A(\omega)=\frac{N}{F\cos\vartheta}\,\sigma(\omega), \tag{18}$$

where $\sigma(\omega)$ equals the ratio of the power $Q(\omega)$ absorbed by a single molecule to the average (over a period of the vibrations) energy flux density in the incident wave:

$$\sigma(\omega)=\frac{8\pi}{c_0E^2}\,Q(\omega),$$

$$Q(\omega)=\frac{1}{2}\,\omega\tilde{E}^\alpha\tilde{E}^\beta\,\frac{1}{n}\sum_{jj'} \operatorname{Im}\,\tilde{\chi}_{jj'}^{\alpha\beta}(0,\omega). \tag{19}$$

Here, $\tilde{E}$ and E are, respectively, the amplitudes, which are related by the Fresnel formulas, of the electric fields on the surface and in free space, c_0 is the velocity of light in free space, and $\tilde{\chi}_{jj'}^{\alpha\beta}(\mathbf{K},\omega)$ is the susceptibility tensor of the system and satisfies the equation

$$\tilde{\chi}_{jj'}^{\alpha\beta}(\mathbf{K},\omega)=\chi_j^{\alpha\beta}(\omega)\,\delta_{jj'} -\chi_j^{\alpha\gamma}(\omega)\sum_{j''} \tilde{V}_{jj''}^{\gamma\lambda}(\mathbf{K})\tilde{\chi}_{j''j'}^{\lambda\beta}(\mathbf{K},\omega), \tag{20}$$

where the polarizability tensor of the jth molecule is

$$\chi_j^{\alpha\beta}(\omega)=-\frac{q_j^2}{m_j}\,\frac{e_j^\alpha e_j^\beta}{\omega^2-\omega_j^2+i0\text{ sign }\omega}. \tag{21}$$

The solution of Eq. (20) with $\mathbf{K}=0$ can be expressed in terms of the eigenvalues and eigenvectors of the problem (16):

$$\tilde{\chi}_{jj'}^{\alpha\beta}(0,\omega)=-\frac{q_jq_{j'}}{\sqrt{m_jm_{j'}}}\,e_j^\alpha e_{j'}^\beta\sum_l \frac{S_{jl}S_{j'l}^*}{\omega^2-\Omega_l^2+i0\text{ sign }\omega}. \tag{22}$$

Substituting Eq. (22) into Eqs. (18) and (19), we obtain the following relation for the total intensity of the lth spectral line:

$$A_l\equiv\int_{\Omega_l-0}^{\Omega_l+0} A(\omega)d\omega=\frac{2\pi^2N}{nc_0F\cos\vartheta}\left|\sum_j \frac{q_j}{\sqrt{m_j}}\,(\epsilon\mathbf{e}_j)S_{jl}\right|^2, \tag{23}$$

where $\epsilon=\tilde{\mathbf{E}}/E$ is the orientation vector of the electric field at the surface and is scaled to the amplitude of the electric field of the infrared radiation in free space. Thus, n molecules in a unit cell of a two-dimensional crystal correspond to n spectral lines. If the molecules are identical (i.e., q_j, m_j, and ω_{0j} do not depend on j) and are subjected to identical static electric fields of neighboring dipoles (ω_j does not depend on j), but the orientations of $\mathbf{e}_j$ are different, then the splitting of a single nondegenerate vibrational state of a free molecule into somewhat differently polarized normal vibrations with formation of a crystal is customarily called Davydov splitting.[11]

In both problems considered, the orientational structures and ground spectroscopic characteristics are determined by the behavior of the Fourier components of the tensor

$\tilde{V}^{\alpha\beta}_{jj'}(\mathbf{K})$ describing the dipole-dipole interactions between the sublattices. The properties of the quantities $\tilde{V}^{\alpha\beta}_{jj}(\mathbf{K})$ for an arbitrary Bravais sublattice have been studied quite well.[4,5,9] For this reason, the problem is to learn how to distinguish most efficiently the quantities $\tilde{V}^{\alpha\beta}_{jj'}(\mathbf{K})$ for $j \neq j'$. We shall show that such intersublattice interactions can be related with the known tensors $\tilde{V}^{\alpha\beta}_{jj}(\mathbf{K})$ for the basis Bravais sublattice. For this we construct a denser Bravais lattice, whose site set $\mathbf{r}=m_1\mathbf{a}_1+m_2\mathbf{a}_2$ includes the set of sites of the compound lattice under consideration. Of course, such a construction is not always possible, but for the most interesting cases of symmetric lattices the main vectors of the Bravais basal sublattice can be represented as integer linear combinations of the main vectors of the dense lattice: $\mathbf{A}_j=n_{j1}\mathbf{a}_1+n_{j2}\mathbf{a}_2$ ($j=1, 2$; $n_{jj'}$ are integers). Then the areas of the unit cells of these lattices will differ by a factor $\det(\hat{n})=n$, and the main vectors of the reciprocal lattices, satisfying the conditions $\mathbf{A}_j\mathbf{B}_{j'} = 2\pi\delta_{jj'}$ and $\mathbf{a}_j\mathbf{b}_{j'} = 2\pi\delta_{jj'}$ will be expressed in terms of one another as linear combinations with rational coefficients:

$$\mathbf{B}_j=\sum_{j'} (\hat{n}^{-1})_{j'j}\mathbf{b}_{j'}. \tag{24}$$

If we now introduce the Fourier components $\tilde{V}^{\alpha\beta}(\mathbf{K})$ of the dipole-dipole interaction tensor on a dense Bravais lattice, then the desired quantities $\tilde{V}^{\alpha\beta}_{jj'}(\mathbf{K})$ for the compound lattice are determined by the expression

$$\tilde{V}^{\alpha\beta}_{jj'}(\mathbf{K})=\frac{1}{n}\sum_{\mathbf{B}} \tilde{V}^{\alpha\beta}(\mathbf{K}+\mathbf{B})\exp(i\mathbf{B}\mathbf{r}_{jj'}), \tag{25}$$

where the summation extends over all integer linear combinations of the vectors $\mathbf{B}_1$ and $\mathbf{B}_2$, falling into the first Brillouin zone of the dense Bravais lattice.

The relation (25) is very convenient both for finding the relations between the values of the tensors $\tilde{V}^{\alpha\beta}(\mathbf{K})$ at different points of the first Brillouin zone and for calculating the interactions of the sublattices of the compound lattice. For a square lattice, it is necessary only to have values of the two lattice sums

$$D_{\mathrm{F}}=-4.516811, \quad D_{\mathrm{A}}=-5.098873, \tag{26}$$

determining the energies $H_0=(1/2)N_0(\mu^2/a^3)D_{\mathrm{F,A}}$, where a is the lattice constant, of the system of dipoles with ferroelectric or antiferroelectric (Fig. 1) ordering in the plane of the lattice.[3] Then the nonzero values $D^{\alpha\beta}(\mathbf{K})\equiv a^3\tilde{V}^{\alpha\beta}(\mathbf{K})$ at symmetric points of the first Brillouin zone and $D^{\alpha\beta}_{jj'}(0) \equiv a^3\tilde{V}^{\alpha\beta}_{jj'}(0)$ with the j sublattices designated as indicated in Fig. 1 will be as follows:

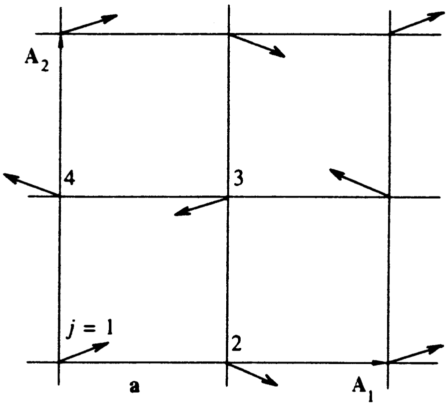

FIG. 1. Ground-state configuration of dipoles on a square lattice and designations of sublattices with identically oriented dipoles.

$$\begin{aligned}
&\hat{D}(0)=D_{\mathrm{F}}\hat{\Gamma}, \quad D^{xx}\left(\frac{1}{2}\,\mathbf{b}_1\right)=\frac{1}{2}\,(1-\sqrt{2})D_{\mathrm{F}}-D_{\mathrm{A}},\\
&D^{yy}\left(\frac{1}{2}\,\mathbf{b}_1\right)=D_{\mathrm{A}},\\
&D^{zz}\left(\frac{1}{2}\,\mathbf{b}_1\right)=-\frac{1}{2}\,(1-\sqrt{2})D_{\mathrm{F}}, \quad \hat{D}\left(\frac{1}{2}\,(\mathbf{b}_1+\mathbf{b}_2)\right)\\
&\quad=(2^{-1/2}-1)D_{\mathrm{F}}\hat{\Gamma},\\
&\hat{D}_{jj}(0)=\frac{1}{8}\,D_{\mathrm{F}}\hat{\Gamma}, \quad \hat{D}_{13}(0)=\hat{D}_{24}(0)=\frac{1}{8}\,(2\sqrt{2}\\
&\quad-1)D_{\mathrm{F}}\hat{\Gamma},\\
&\hat{D}_{14}(0)=\hat{D}_{23}(0)=\frac{1}{4}\left[(2-2^{-1/2})D_{\mathrm{F}}\hat{\Gamma}+\left(\frac{1}{2}\,(1\right.\right.\\
&\quad\left.\left.-\sqrt{2})D_{\mathrm{F}}-2D_{\mathrm{A}}\right)\hat{\Lambda}\right],\\
&\hat{D}_{12}(0)=\hat{D}_{34}(0)=\frac{1}{4}\left[(2-2^{-1/2})D_{\mathrm{F}}\hat{\Gamma}-\left(\frac{1}{2}\,(1\right.\right.\\
&\quad\left.\left.-\sqrt{2})D_{\mathrm{F}}-2D_{\mathrm{A}}\right)\hat{\Lambda}\right],\\
&\hat{\Gamma}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix}, \quad \hat{\Lambda}=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&0\end{pmatrix}.
\end{aligned} \tag{27}$$

For the structure, displayed in Fig. 1, of the projections of the dipole moments on the plane of the square lattice, corresponding to the ground state,

$$\begin{aligned}
&\mathbf{e}_1=(\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta),\\
&\mathbf{e}_2=(\sin\theta\cos\varphi,-\sin\theta\sin\varphi,\cos\theta),\\
&\mathbf{e}_3=(-\sin\theta\cos\varphi,-\sin\theta\sin\varphi,\cos\theta),\\
&\mathbf{e}_4=(-\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta),
\end{aligned} \tag{28}$$

where 90°—θ is the tilt angle of the dipoles with respect to the plane of the lattice, substituting Eqs. (27) and (28) into Eqs. (14)–(16) and (23) gives the following squared frequencies and integral intensities of the spectral lines:

$$\begin{aligned}
&\Omega_1^2=\omega_0^2[1+(\chi/a^3)\,(1+\kappa)(-2D_{\mathrm{F}}\cos^2\theta\\
&\quad+D_{\mathrm{A}}\sin^2\theta)], \quad A_1\propto\epsilon_z^2\cos^2\theta,\\
&\Omega_2^2=\omega_0^2[1+\,(\chi/a^3)(1+\kappa)(-2D_{\mathrm{F}}\cos^2\theta+D_{\mathrm{A}}\sin^2\theta)
\end{aligned}$$

$$-\tfrac{1}{2}(\chi/a^3)(1-\sqrt{2})D_{\mathrm{F}}\sin^2\theta],\quad A_2=0,$$

$$\Omega_3^2=\omega_0^2\{1+(\chi/a^3)\kappa(-2D_{\mathrm{F}}\cos^2\theta+D_{\mathrm{A}}\sin^2\theta)$$
$$-\tfrac{1}{2}(\chi/a^3)(1-\sqrt{2})D_{\mathrm{F}}\cos^2\theta+(\chi/a^3)D_{\mathrm{F}}[\cos^2\varphi$$
$$+(2^{-1/2}-1)\sin^2\varphi]\sin^2\theta\},\tag{29}$$

$$A_3\propto\epsilon_x^2\sin^2\theta\cos^2\varphi,$$

$$\Omega_4^2=\omega_0^2\{1+(\chi/a^3)\kappa(-2D_{\mathrm{F}}\cos^2\theta+D_{\mathrm{A}}\sin^2\theta)$$
$$-\tfrac{1}{2}(\chi/a^3)(1-\sqrt{2})D_{\mathrm{F}}\cos^2\theta+(\chi/a^3)D_{\mathrm{F}}[\sin^2\varphi$$
$$+(2^{-1/2}-1)\cos^2\varphi]\sin^2\theta\},$$

$$A_4\propto\epsilon_y^2\sin^2\theta\sin^2\varphi,$$

where $\chi=q^2/(m\omega_0^2)$ is the vibrational polarizability of a molecule, and $\kappa=2\alpha\mu/qk$ is a dimensionless parameter, describing the static renormalization of the frequency in the presence of the cubic anharmonicity α. The unitary matrix representing the transformation to normal coordinates has the form

$$S_{jl}=\frac{1}{2}\begin{pmatrix}1 & 1 & 1 & 1\\ 1 & -1 & 1 & -1\\ 1 & 1 & -1 & -1\\ 1 & -1 & -1 & 1\end{pmatrix}.\tag{30}$$

When the relations (27) are taken into account, the expressions (29) for the allowed absorption lines ($A_l\neq 0$) in the infrared spectra are identical to those obtained in Ref. 12 by a different method, which does not employ a sublattice description. The magnitudes of the Davydov splitting are determined by the differences of the squared frequencies (29) and do not depend on the static renormalization of the frequencies. For a structure with $\varphi=0$, corresponding to the system CO/NaCl(100),[6] the relations (29) give good agreement with the observed magnitude of the Davydov splitting.[12]

We now illustrate the operation of the identity (25) for the example of a complex hexagonal lattice with the hexagon edgelength equal to a. The basis vectors of the basis triangular sublattice $\mathbf{A}_1=\sqrt{3}a(1,0,0)$ and $\mathbf{A}_2=\sqrt{3}a(1/2,\sqrt{3}/2,0)$ can be expressed in terms of the basis vectors of the dense triangular lattice $\mathbf{a}_1=a(0,-1,0)$ and $\mathbf{a}_2=a(\sqrt{3}/2,-1/2,0)$ as follows: $\mathbf{A}_1=2\mathbf{a}_2-\mathbf{a}_1$ and $\mathbf{A}_2=\mathbf{a}_2-2\mathbf{a}_1$ (Fig. 2a). Then we have $\mathbf{r}_{21}=a(\sqrt{3}/2,1/2,0)=\mathbf{a}_2-\mathbf{a}_1$, and all sites of the compound lattice are included in the site set of the dense Bravais lattice. The basis vectors of the reciprocal lattices are related by the relations $\mathbf{B}_1=(\mathbf{b}_1+2\mathbf{b}_2)/3$ and $\mathbf{B}_2=-(2\mathbf{b}_1+\mathbf{b}_2)/3$, so that the corresponding first Brillouin zones have the form displayed in Fig. 2b and the summation in Eq. (25) is limited to the vectors $\mathbf{B}=-\mathbf{B}_2$, 0, and $\mathbf{B}_2$. For this reason,

$$\tilde V_{11}^{\alpha\beta}(\mathbf{K})=\tilde V_{22}^{\alpha\beta}(\mathbf{K})=\frac{1}{3}[\tilde V^{\alpha\beta}(\mathbf{K})+\tilde V^{\alpha\beta}(\mathbf{K}+\mathbf{B}_2)$$
$$+\tilde V^{\alpha\beta}(\mathbf{K}-\mathbf{B}_2)],\tag{31}$$

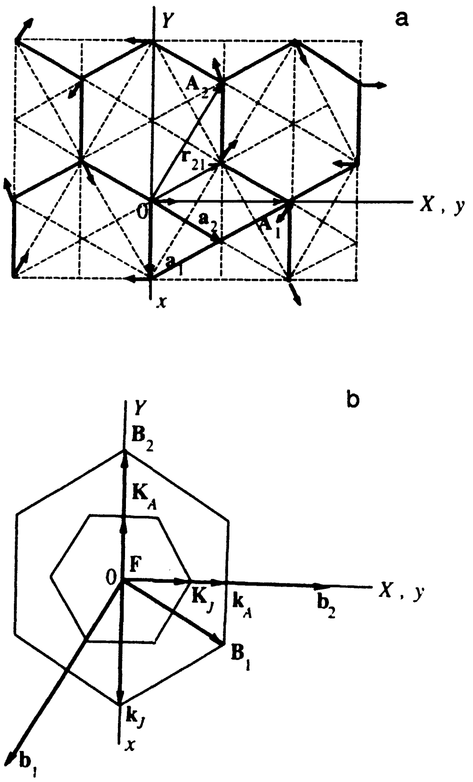

FIG. 2. a—Ground-state configuration of dipoles on a compound hexagonal lattice and the corresponding basis and dense triangular lattices. b—First Brillouin zones for the reciprocal basis and dense lattices.

$$\tilde V_{21}^{\alpha\beta}(\mathbf{K})=[\tilde V_{12}^{\alpha\beta}(\mathbf{K})]^*=\frac{1}{3}\left\{\tilde V^{\alpha\beta}(\mathbf{K})-\frac{1}{2}[\tilde V^{\alpha\beta}(\mathbf{K}+\mathbf{B}_2)\right.$$
$$+\tilde V^{\alpha\beta}(\mathbf{K}-\mathbf{B}_2)]+i\frac{\sqrt{3}}{2}[\tilde V^{\alpha\beta}(\mathbf{K}+\mathbf{B}_2)$$
$$\left.-\tilde V^{\alpha\beta}(\mathbf{K}-\mathbf{B}_2)]\right\}.\tag{32}$$

The dense Bravais lattice is the same basis triangular sublattice, but is turned clockwise by 90° around the Z axis. Introducing the corresponding rotation matrix $\hat O$, we obtain the following important identity:

$$\hat{\tilde V}_{jj}(\mathbf{K})=3^{-3/2}\hat O\hat{\tilde V}(\sqrt{3}\hat O^{-1}\mathbf{K})\hat O^{-1},\tag{33}$$

which, together with the relation (31), makes it possible to associate the values of $\tilde V^{\alpha\beta}(\mathbf{K})$ at different points of the first Brillouin zone. In particular, at the symmetric points $\mathbf{K}=0$, $\mathbf{k}_{\mathrm{A}}=\mathbf{b}_2/2$, $\mathbf{k}_{\mathrm{J}}=-\mathbf{B}_2$ (Fig. 2b) and at $\mathbf{K}=\mathbf{K}_{\mathrm{J}}=\mathbf{b}_2/3$ for $D^{\alpha\beta}(\mathbf{K})=a^3\tilde V^{\alpha\beta}(\mathbf{K})$ we obtain

$$D^{\alpha\beta}(0)=D_{\mathrm{F}}\delta_{\alpha\beta},\quad D^{\alpha\beta}(\mathbf{k}_{\mathrm{J}})=\tfrac{1}{2}(3^{1/2}-1)D_{\mathrm{F}}\delta_{\alpha\beta},$$
$$\alpha,\beta=x,y,$$
$$D^{xx}(\mathbf{k}_{\mathrm{A}})=D_{\mathrm{A}},\quad D^{yy}(\mathbf{k}_{\mathrm{A}})=-D_A-\tfrac{1}{3}D_{\mathrm{F}},\quad D^{xy}(\mathbf{k}_{\mathrm{A}})=0,$$
$$D^{xx}(\mathbf{K}_{\mathrm{J}})=-4.453809,\quad D^{yy}(\mathbf{K}_{\mathrm{J}})=3^{-3/2}(3^{-1/2}-1)D_{\mathrm{F}}$$
$$-D^{xx}(\mathbf{K}_{\mathrm{J}});D^{xy}(\mathbf{K}_{\mathrm{J}})=0,\tag{34}$$
$$D^{zz}(\mathbf{K})=-D^{xx}(\mathbf{K})-D^{yy}(\mathbf{K}),$$

where $D_F=-5.517088$ and $D_A=-4.094910$ determine the energies of the ferroelectric and antiferroelectric states on a triangular lattice of dipoles.[3] Now, the following values are obtained with the help of the relations (32) for $D_{21}^{\alpha\beta}(\mathbf{K})$ with $\mathbf{K}=0$, $\mathbf{K}_A=\mathbf{B}_2/2$, and $\mathbf{K}_J=\mathbf{b}_2/3$ (Fig. 2b):

$$D_{21}^{\alpha\beta}(0)=\frac{1}{2}(1-3^{-3/2})D_F\delta_{\alpha\beta}, \quad D_{21}^{XX}(\mathbf{K}_A)=\frac{1}{2}\left[(1+3^{-3/2})D_A+\frac{1}{3}D_F\right]\exp\left(-\frac{\pi i}{3}\right),$$

$$D_{21}^{YY}(\mathbf{K}_A)=-\frac{1}{2}[(1+3^{-3/2})D_A+3^{-5/2}D_F]\times\exp\left(-\frac{\pi i}{3}\right), \quad D_{21}^{XY}(\mathbf{K}_A)=0,$$

$$D_{21}^{XX}(\mathbf{K}_J)=-D_{21}^{YY}(\mathbf{K}_J)=-iD_{21}^{XY}(\mathbf{K}_J)=\frac{1}{4}\,3^{-3/2}(3^{-1/2}-1)D_F-\frac{1}{2}\,D^{xx}(\mathbf{K}_J),$$

$$D_{21}^{ZZ}(\mathbf{K})=-D_{21}^{XX}(\mathbf{K})-D_{21}^{YY}(\mathbf{K}). \tag{35}$$

The eigenvalues of the tensor $D_{jj'}^{\alpha\beta}(K)=a^3\tilde{V}_{jj'}^{\alpha\beta}(\mathbf{K})$ at symmetric points of the first Brillouin zone, which are determined by Eq. (7), assume the following form:

$$D_1^1(0)=D_1^2(0)=-\frac{1}{2}\,D_1^3(0)=\frac{1}{2}\,(1+3^{-3/2})D_F=-3.289426,$$

$$D_2^1(0)=D_2^2(0)=-\frac{1}{2}\,D_2^3(0)=\frac{1}{2}\,(3^{-1/2}-1)D_F=1.165898,$$

$$D_1^1(\mathbf{K}_A)=\frac{1}{2}\left[\frac{1}{3}\,D_F+(1+3^{-1/2})D_A\right]=-4.149068,$$

$$D_1^2(\mathbf{K}_A)=-\frac{1}{2}\,[3^{-5/2}D_F-(1-3^{-3/2})D_A]=-1.476461,$$

$$D_2^1(\mathbf{K}_A)=-\frac{1}{2}\left[\frac{1}{3}\,D_F+(1-3^{-3/2})D_A\right]=2.572937, \tag{36}$$

$$D_2^2(\mathbf{K}_A)=-\frac{1}{2}\,[3^{-3/2}D_F+(1+3^{-1/2})D_A]=3.760436,$$

$$D_1^3(\mathbf{K}_A)=-D_1^1(\mathbf{K}_A)-D_2^2(\mathbf{K}_A), \quad D_2^3(\mathbf{K}_A)=-D_1^2(\mathbf{K}_A)-D_2^1(\mathbf{K}_A),$$

$$D_1^1(\mathbf{K}_J)=D^{xx}(\mathbf{K}_J)=-4.453809, \quad D_2^2(\mathbf{K}_J)=D^{yy}(\mathbf{K}_J)=4.902564,$$

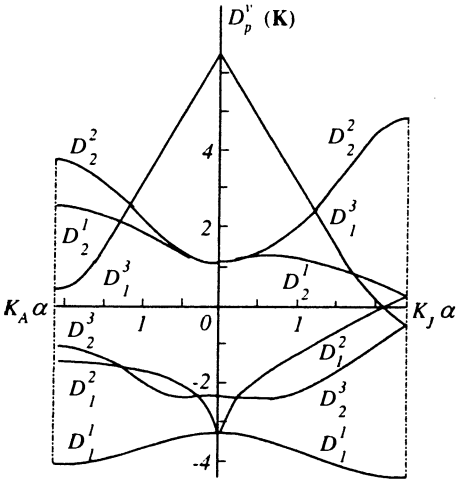

FIG. 3. Eigenvalues $D_p^\nu(\mathbf{K})$ of the Fourier components of the dipole-dipole interaction tensor on a hexagonal lattice as a function of the wave vector $\mathbf{K}$, determined in the first Brillouin zone of the basal sublattice.

$$D_1^2(\mathbf{K}_J)=D_1^2(\mathbf{K}_J)=-\frac{1}{2}\,D_1^3(\mathbf{K}_J)=-\frac{1}{2}\,D_2^3(\mathbf{K}_J)=\frac{1}{2}\,3^{-3/2}(3^{-1/2}-1)D_F=0.224377.$$

The functions $D_p^\nu(\mathbf{K})$ in the symmetric directions of the first Brillouin zone are displayed in Fig. 3. The lowest value $D_1^1(\mathbf{K}_J)$ determines the energy $H_0=1/2N(\mu^2/a^3)D_1^1(\mathbf{K}_J)$ of the one-parameter degenerate (with respect to the angle φ) ground state of a system with the following configurations of dipole moments:

$$\mathbf{e}_{\mathbf{R}1}=\{\cos[(\mathbf{K}_J\mathbf{R})+\varphi],\ \sin[(\mathbf{K}_J\mathbf{R})+\varphi],0\},$$

$$\mathbf{e}_{\mathbf{R}2}=\left[-\cos\left[(\mathbf{K}_J\mathbf{R})+\frac{2\pi}{3}+\varphi\right],\ \sin\left[(\mathbf{K}_J\mathbf{R})+\frac{2\pi}{3}+\varphi\right],0\right], \tag{37}$$

displayed in Fig. 2a. It is interesting that the same configuration of dipole moments in the ground state with $D_1^1(\mathbf{K}_J)=-9/2$ is obtained when the dipole-dipole interactions are taken into account in the simplest nearest-neighbor approximation,[13] while for a triangular lattice of dipoles the short- and long-range models give ground states with qualitatively different structures.[3] Numerical calculations of the ground-state energy taking into account the long-range interaction between 72 dipoles, surrounded by 48 similar dipole configurations, led in Ref. 13 to the value $H_0=-2.2269N\mu^2/a^3$, very close to the exact value $(D_1^1(\mathbf{K}_J)/2=-2.226905)$. We note that in Ref. 14 the ground state of dipoles on a hexagonal lattice was analyzed in terms of chain structures. This limitation on the possible types of dipole orientations made it impossible to find the most advantageous antiferroelectric vortex state $D_1^1(\mathbf{K}_J)$ and revealed only the layered antiferroelectric state $D_1^1(\mathbf{K}_A)$.

We now analyze the effect of thermodynamic fluctuations of the order parameter on the ground state of dipoles on a hexagonal lattice. Just as for a square lattice,[3,7,15] two factors materialize here simultaneously: the quadratic asymptotic behavior of the minimum branch of the eigenvalues $D_1^1(\mathbf{K})$ around the ground state with $\mathbf{K}=\mathbf{K}_\mathrm{J}$ and its one-parameter degeneracy with respect to the angular variable. As shown in Ref. 15 and confirmed in Ref. 16 by Monte Carlo modeling on a square lattice, because of these factors a low-temperature dipole system is in a Berezinskiĭ–Kosterlitz–Thouless phase. Removal of degeneracy by local potentials or multipole corrections will stabilize the long-range order, as in the case of a square lattice of dipoles.[17]

The curves $D_p^\nu(\mathbf{K})$ in Fig. 3 determine six branches of vibrations of the charges, which can be displaced relative to the sites of a hexagonal lattice. Since the hexagonal lattices are realized on the basal face of graphite, for which a large volume of experimental data on adsorption has been accumulated,[18,19] here it is useful to give the computed frequencies of the radial vibrations of adsorbed polar molecules that should be observed in the infrared spectra. The adsorption potentials can force the dipole moments of the adsorbed molecules from the lattice plane,[6] so that the X and Y components of the vectors in Eq. (37) are premultiplied by $\sin\theta$, and the Z components will be $\cos\theta$. Using as a basis the similar calculation for a square lattice performed in Ref. 12, we obtain

$$\begin{aligned}\Omega_Z^2&=\omega_0^2[1+(\chi/a^3)(1+\kappa)(D_1^3(0)\cos^2\theta\\&\quad+D_1^1(\mathbf{K}_\mathrm{J})\sin^2\theta)],\\ \Omega_X^2&=\Omega_Y^2=\omega_0^2[1+(\chi/a^3)\kappa(D_1^3(0)\cos^2\theta\\&\quad+D_1^1(\mathbf{K}_\mathrm{J})\sin^2\theta)+(\chi/a^3)D_1^3(\mathbf{K}_\mathrm{J})\cos^2\theta+\tfrac{1}{2}(\chi/a^3)\\&\quad\times[D_1^1(0)+D_1^2(\mathbf{K}_\mathrm{J})]\sin^2\theta].\end{aligned}\tag{38}$$

Here the indices X, Y, Z indicate polarization of the corresponding vibration, and the notations agree with those adopted in the expressions (29). The magnitude of the Davydov splitting of the spectral lines

$$\begin{aligned}\Delta\Omega_{\mathrm{Dav}}&\simeq\frac{1}{2\omega_0}(\Omega_Z^2-\Omega_X^2)=\frac{\chi\omega_0}{2a^3}\Bigg\{[D_1^3(0)\\&\quad-D_1^3(\mathbf{K}_\mathrm{J})]\cos^2\theta-\left[\frac{1}{2}(D_1^1(0)+D_1^2(\mathbf{K}_\mathrm{J}))\right.\\&\quad\left.-D_1^1(\mathbf{K}_\mathrm{J})\right]\sin^2\theta\Bigg\}\end{aligned}\tag{39}$$

is determined by the values of $D_p^\nu(\mathbf{K})$ (36) at symmetric points of the first Brillouin zone and is described by the lateral interactions, inclusively, of the dynamic dipole moments of adsorbed molecules.

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