

Translational-rotational interaction in dynamics and thermodynamics of 2D atomic crystal with molecular impurity

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The interaction between the rotational degrees of freedom of a diatomic molecular impurity and the phonon excitations of a two-dimensional atomic matrix commensurate with a substrate is investigated theoretically. It is shown, that the translational-rotational interaction changes the form of the rotational kinetic energy operator as compared to the corresponding expression for a free rotator, and also renormalizes the parameters of the crystal field without change in its initial form. The contribution of the impurity rotational degrees of freedom to the low-temperature heat capacity for a dilute solution of diatomic molecules in an atomic two-dimensional matrix is calculated. The possibility of experimental observation of the effects obtained is discussed.

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1. Introduction

Two-dimensional (2D) cryocrystals on substrates of different kind are of great theoretical and experimental interest due to the wide variety of physical phenomena (in thermodynamics, excitation spectra, and magnetism) they demonstrate. For 2D monoatomic crystals containing molecular impurities the interaction between rotational degrees of freedom and matrix phonon excitations, so-called translational-rotational interaction (TRI) [1], is an important factor controlling the dynamics of the impurity molecules. Since an impurity in a 2D solution moves in the low symmetry potential, its dynamics appears to be substantially more complex than that in a 3D system [2]. This can appreciably affect all physical characteristics, in particular, low-temperature heat capacity, and also can lead to some effects not found in the 3D case. Theoretically, the problem of TRI in the 2D cryosolutions has not been sufficiently studied.

The aim of the present paper is to investigate theoretically the effect of the phonon excitations on rotational dynamics of a diatomic impurity in a 2D close-packed atomic matrix and the impurity heat capacity at low temperatures.

2. Hamiltonian

Let us consider a diatomic homonuclear substitutional impurity with mass M and internuclear distance $2d$ in the two-dimensional close-packed monoatomic matrix (the coordination number in the layer $z_1 = 6$), placed on a rigid substrate. The matrix and the substrate structures are supposed to be commensurate, so that a monolayer atom has z_2 nearest neighbors in the substrate. The substrate forms either triangular ($z_2 = 3$) or honeycomb ($z_2 = 6$) lattice. For definiteness we assume, that the impurity is located at the origin, the OZ axis is chosen normal to the layer and is directed from the substrate, and the OX and OY axes are oriented in the matrix plane. We restrict our consideration to the case of the isotopic impurity.

Assuming that the displacement \mathbf{u}_f of the impurity center of inertia from its equilibrium position is small in comparison with the distances to the nearest neighbors both in the layer, R_1 , and in the substrate, R_2 , and taking into account smallness of d/R_i ($i = 1, 2$), the total Hamiltonian of the system can be written as

$$H = -B\Delta_{\theta,\varphi} + H_{\text{ph}} + H_c + H_{\text{int}}, \quad (1)$$

where the first term is the kinetic energy of the impurity molecule, $B = \hbar^2/(2I)$ is the rotational constant of the molecule, $I = Md^2$ is its moment of inertia,

$\Delta_{\theta,\varphi}$ is the angular part of the Laplacian, θ and φ are azimuth and polar angle specifying the molecule axis orientation.

The Hamiltonian of the phonon subsystem H_{ph} has the form

$$H_{\text{ph}} = \frac{1}{2} \sum_{\mathbf{v}} \left(\frac{|\pi_{\mathbf{v}}|^2}{m} + m\Omega_{\mathbf{v}}^2 |\xi_{\mathbf{v}}|^2 \right) + \frac{\varepsilon}{2MN} \sum_{\mathbf{v}, \mathbf{v}'} (\mathbf{e}_{\mathbf{v}}, \mathbf{e}_{\mathbf{v}'}) \pi_{\mathbf{v}} \pi_{\mathbf{v}'}^*,$$

where $\mathbf{e}_{\mathbf{v}}$ and $\Omega_{\mathbf{v}}$ are the unit polarization vectors and frequencies of a pure monolayer phonon excitations, respectively, $\mathbf{v} = (\mathbf{k}, \alpha)$, \mathbf{k} is a two-dimensional wave vector, $\alpha = l, t, z$; l, t specify the longitudinal and transverse modes polarized in the layer plane (in-plane modes), and z is the index for the mode polarized normally to the layer (out-of-plane mode), $\xi_{\mathbf{v}}$ are coefficients in a series expansion of $\mathbf{u}_{\mathbf{f}}$ in the unit polarization vectors $\mathbf{e}_{\mathbf{v}}$, $\pi_{\mathbf{v}} = -i\hbar \partial / \partial \xi_{\mathbf{v}}$, m is the mass of a matrix atom, $\varepsilon = (m - M)/m$ is the mass defect, N is the number of sites in the layer. For a pure crystal in the commensurate regime all the phonon spectrum branches have gaps: equal Δ for the in-plane modes and Δ_z for the out-of-plane mode with $\Delta_z > \Delta$. As a rule, the z -mode is practically dispersionless [3]. Explicit forms of $\Omega_{\mathbf{v}}$ for the system under consideration can be found in [3,4].

With an accuracy to $(d/R_i)^4$ the crystal field H_c has the form

$$H_c = -\frac{G_0}{2} \omega_z^2 + \frac{1}{2} [G_1 \omega_z^4 + \Delta_{z23} G_2 \omega_y \omega_z (\omega_y^2 - 3\omega_x^2)]. \quad (2)$$

Here $\mathbf{w} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, Δ_{ij} is the Kronecker symbol,

$$G_0 = d^2 \left\{ \sum_{i=1,2} z_i \mathcal{M}_i - z_2 (1 - b^2) [3\mathcal{M}_2 + d^2 (5b^2 - 2) \mathcal{P}_2] \right\},$$

$$G_1 = \frac{d^4}{2} \left[\sum_{i=1,2} z_i \mathcal{P}_i + \frac{5}{3} z_2 (1 - b^2) (1 - 7b^2) \mathcal{P}_2 \right],$$

$$G_2 = \frac{4d^4}{3} z_2 b^3 \sqrt{1 - b^2} \mathcal{P}_2,$$

$$\mathcal{M}_i = A_i + \frac{d^2}{8} R_i \frac{d}{dR_i} \left(\frac{1}{R_i} \frac{dA_i}{dR_i} \right),$$

$$\mathcal{P}_i = \frac{1}{8} R_i \frac{d}{dR_i} \left(R_i^3 \frac{d}{dR_i} \frac{A_i}{R_i^4} \right),$$

$$A_i = R_i \frac{d}{dR_i} \left(\frac{1}{R_i} \frac{dV_i}{dR_i} \right),$$

parameter b is equal to $R_1/(\sqrt{3}R_2)$ and $R_1/(3R_2)$ for the substrates with triangular and honeycomb lattices respectively; V_i are atom-atom potentials describing interactions between the impurity and matrix atoms ($i = 1$) and between the impurity and substrate atoms ($i = 2$).

The first two terms in (2) are determined by both the matrix and the substrate, whereas the last term with a lower symmetry (of group S_6) is associated only with the crystal field of the substrate. The analysis of $G_{0,1}$ shows that the substrate field makes the impurity lie down in the layer, while the matrix field tends to orientate it perpendicular to the substrate. Thus, the equilibrium position of the impurity is determined by a competition between the two factors.

Interaction between the phonon subsystem and the rotational degrees of freedom of the impurity is described by the following Hamiltonian [5,6]:

$$H_{\text{int}} = -\frac{d^2}{2\sqrt{N}} \sum_{\mathbf{v}} (f_{\mathbf{v}}^* \xi_{\mathbf{v}} + \text{c. c.}), \quad f_{\mathbf{v}} = \Gamma_{\mathbf{v}}^{\alpha\beta} Q_{\alpha\beta} + C_{\mathbf{v}}. \quad (3)$$

Here $Q_{\alpha\beta} = \omega_{\alpha} \omega_{\beta} - \Delta_{\alpha\beta}/3$ is the dimensionless quadrupole moment of the impurity molecule,

$$\Gamma_{\mathbf{v}}^{\alpha\beta} = s^{\alpha\beta\gamma}(\mathbf{k}) e_{\mathbf{v}}^{\gamma} + 2h^{\alpha}(\mathbf{k}) e_{\mathbf{v}}^{\beta},$$

$$C_{\mathbf{v}} = \frac{1}{3} [s^{\alpha\alpha\gamma}(\mathbf{k}) + 5h^{\gamma}(\mathbf{k})] e_{\mathbf{v}}^{\gamma},$$

$$s^{\alpha\beta\gamma}(\mathbf{k}) = \mathcal{K}_1 \sum_{\bar{\delta}} \delta^{\alpha} \delta^{\beta} \delta^{\gamma} \exp(i\mathbf{k}\bar{\delta}R_1) + \mathcal{K}_2 \sum_{\bar{\Delta}} \Delta^{\alpha} \Delta^{\beta} \Delta^{\gamma}, \quad (4)$$

$$h^{\alpha}(\mathbf{k}) = \kappa_1 \sum_{\bar{\delta}} \delta^{\alpha} \exp(i\mathbf{k}\bar{\delta}R_1) + \kappa_2 \sum_{\bar{\Delta}} \Delta^{\alpha},$$

$$\mathcal{K}_i = R_i^2 \frac{d}{dR_i} \frac{A_i}{R_i^2}, \quad \kappa_i = \frac{A_i}{R_i},$$

$\bar{\delta}$, $\bar{\Delta}$ are unit vectors directed to the nearest neighbours in the layer and in the substrate.

3. Impurity dynamics

Let us consider the effect of interaction between the rotational degrees of freedom of the impurity and the matrix phonon excitations on the character of the molecule motion. To do this we use the functional integration method [7]. Within an insignificant normalizing factor the partition function Z of the system under study has the following form

$$Z = \int D[\xi(\tau)] D[\mathbf{w}(\tau)] \exp(S/\hbar), \quad (5)$$

where S is the total action

$$S = \int_0^{\hbar/T} d\tau L(\tau), \quad L = L_{\text{ph}} + L_{\text{rot}} + L_{\text{int}} + L_c,$$

$$L_{\text{ph}} = -\frac{m}{2} \sum_{\mathbf{v}} \left[|\dot{\xi}_{\mathbf{v}}|^2 + \Omega_{\mathbf{v}}^2 |\xi_{\mathbf{v}}|^2 - \frac{\varepsilon}{N} \sum_{\mathbf{v}'} (\mathbf{e}_{\mathbf{v}}, \mathbf{e}_{\mathbf{v}'}) \dot{\xi}_{\mathbf{v}} \dot{\xi}_{\mathbf{v}'}^* \right],$$

$$L_{\text{rot}} = -\frac{I}{2} \left(\frac{\partial \mathbf{w}}{\partial \tau} \right)^2 = -\frac{I}{2} (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta),$$

$$L_{\text{int}} + L_c = -(H_{\text{int}} + H_c),$$

τ is the imaginary time, the Boltzmann constant $k_B = 1$. The dots denote differentiation with respect to τ .

After integration over the phonon variables, the partition function (5) takes the form of the product $Z = Z_{\text{ph}} Z_1$. The factor Z_{ph} is the phonon partition function of the 2D crystal, and Z_1 corresponds to the rotational motion of the molecule with regard to influence on it of the phonon subsystem. For real systems rotational levels of a molecular impurity are, as a rule, low-energetic, and, hence, specific effects caused by rotational excitations make themselves evident at extremely low temperatures. Besides, due to the presence of an isotopic impurity there appear local ω_{loc} and quasi-local frequencies in the phonon spectrum [8]. For the light impurity ($\varepsilon > 0$) the local levels lay above the top edge of the continuous spectrum, whereas for the heavy impurity ($\varepsilon < 0$) these levels are situated below its bottom edge, i.e. in the gap. Our interest here is in the temperature range $T \leq \hbar\Delta$, $\hbar\omega_{\text{loc}}$.

Within the present approximation TRI gives rise to additional terms of the order $(d/R_i)^4$ in the crystal field

$$\begin{aligned} H_c &\rightarrow \tilde{H}_c = H_c + \Delta H_c, \\ \Delta H_c &= -\frac{d^4}{2mN} \sum_{\mathbf{v}} \frac{|f_{\mathbf{v}}|^2}{\Omega_{\mathbf{v}}^2}, \end{aligned} \quad (6)$$

and also in the kinetic energy operator

$$\begin{aligned} H_{\text{rot}} &\rightarrow \tilde{H}_{\text{rot}} = H_{\text{rot}} + \Delta H_{\text{rot}}, \\ \Delta H_{\text{rot}} &= \frac{d^4}{2m} \left\{ \frac{1}{N} \sum_{\mathbf{v}} \frac{|f_{\mathbf{v}}|^2}{\Omega_{\mathbf{v}}^4} - \varepsilon \left| \frac{1}{N} \sum_{\mathbf{v}} \frac{f_{\mathbf{v}} \mathbf{e}_{\mathbf{v}}}{\Omega_{\mathbf{v}}^2} \right|^2 \right\}. \end{aligned} \quad (7)$$

To analyze Eqs. (6), (7) it is necessary to calculate sums (4) over the nearest neighbors in the layer. For lattices with the coordination number large enough an effective way of the calculation is to replace the summation by integration over a circle of unit radius [3,4]. Such a replacement is quite justified since the

corrections (6), (7) are integral characteristics (obtained by the summation over \mathbf{k} in the Brillouin zone).

The interaction between the impurity rotational degrees of freedom and phonons does not modify the general form of the crystal field (2), but renormalizes its coefficients:

$$G_i \rightarrow \tilde{G}_i = G_i + \Delta G_i, \quad \Delta G_i = \Delta G_i^L + \Delta G_i^S, \quad i = 0, 1, 2,$$

where the indices L and S specify contributions caused mainly by the impurity interaction with the matrix atoms and substrate atoms, respectively:

$$\Delta G_0^L = -\frac{z_1^2 d^4}{6m} (\mathcal{A}_1 + 3\mathcal{B}_1 + C_1),$$

$$\Delta G_1^L = -\frac{z_1^2 d^4}{4m} (\mathcal{A}_1 + \mathcal{B}_1),$$

$$\Delta G_0^S = \frac{z_2^2 d^4}{2m} [(2K_0^2 - K_2^2 \Delta_{z_2,3}) s_{\perp}^{(1)} - K_0 K_1 s_z^{(1)}],$$

$$\Delta G_1^S = \frac{z_2^2 d^4}{4m} [(4K_0^2 - K_2^2 \Delta_{z_2,3}) s_{\perp}^{(1)} - K_1^2 s_z^{(1)}],$$

$$\Delta G_2^S = -\frac{z_2^2 d^4}{m} K_0 K_2 s_{\perp}^{(1)}.$$

Here

$$\mathcal{A}_m = \frac{1}{N} \sum_{\mathbf{k}} \frac{\alpha_1^2}{\Omega_l^{2m}},$$

$$\mathcal{B}_m = \frac{1}{8N} \sum_{\mathbf{k}} \left[\frac{(\alpha_2 - \alpha_3)^2}{\Omega_l^{2m}} + \frac{(\alpha_2 + \alpha_3)^2}{\Omega_t^{2m}} \right],$$

$$C_m = \frac{1}{N} \sum_{\mathbf{k}} \frac{\alpha_1 (3\alpha_2 - \alpha_1)}{\Omega_l^{2m}}, \quad \alpha_1 = (\mathcal{K}_1 + 2\kappa_1) J_1(kR_1),$$

$$\alpha_2 = (\mathcal{K}_1 + 4\kappa_1) J_1(kR_1),$$

$$\alpha_3 = \mathcal{K}_1 J_3(kR_1), \quad K_0 = \sqrt{1 - b^2} (b^2 \mathcal{K}_2 + 2\kappa_2),$$

$$K_1 = \sqrt{1 - b^2} [(3b^2 - 2)\mathcal{K}_2 - 4\kappa_2], \quad K_2 = \frac{b^3}{2} \mathcal{K}_2,$$

$$s_{\perp}^{(m)} = \frac{1}{2N} \sum_{\mathbf{k}, \alpha=l,t} \frac{1}{\Omega_{\alpha}^{2m}}, \quad s_z^{(m)} = \frac{1}{N} \sum_{\mathbf{k}} \frac{1}{\Omega_z^{2m}}.$$

where $J_n(x)$ is the Bessel function. By symmetry reasoning the impurity interaction with the neighbors in the layer results only in the renormalization of the coefficients G_0 and G_1 in (2). It can be shown, that for short-range potentials the values ΔG_0^L and ΔG_1^L are negative, whereas ΔG_0^S is positive.

The contributions to the crystal field both from the monolayer and from the substrate decrease in ampli-

tude due to TRI. Such a result is physically quite clear. The rotational motion is mainly affected by high-frequency phonons creating maximal deformations in the first coordination sphere around the impurity. The considered situation is close to the known problem on the motion of a particle in a fast-oscillating field where after averaging on oscillations the depth of the initial potential well effectively decreases [9].

Rather different situation takes place for the kinetic energy. The TRI results in essential change of H_{rot} form. After appropriate transformations the effective kinetic energy (7) can be represented as a generalized quadratic form of the angular velocity components \dot{w}_i with coefficients dependent on the molecular orientation:

$$\Delta H_{\text{rot}} = \frac{1}{2} (\Delta I_{\perp} \dot{w}_{\perp}^2 + \Delta I_z \dot{w}_z^2 + \Delta_{z_2,3} \Delta I_{ij} \dot{w}_i \dot{w}_j),$$

$$\dot{\mathbf{w}} = (w_x, w_y, 0). \quad (8)$$

The additives $\Delta I_{\perp,z}$ to the impurity moment of inertia are

$$\Delta I_{\perp,z} = \Delta I_{\perp,z}^L + \Delta I_{\perp,z}^S,$$

$$\Delta I_{\perp}^L = z_1^2 \frac{d^4}{m} \mathcal{B}_2 w_{\perp}^2,$$

$$\Delta I_z^L = z_1^2 \frac{d^4}{m} \mathcal{A}_2 w_z^2,$$

$$\Delta I_{\perp}^S = \frac{z_2^2 d^4}{m} \zeta_{\perp} (K_0^2 w_z^2 + \Delta_{z_2,3} K_2^2 w_{\perp}^2),$$

$$\Delta I_z^S = \frac{z_2^2 d^4}{m} [K_0^2 \zeta_{\perp} (1 - 3w_z^2) + K_1^2 \zeta_z w_z^2],$$

where

$$\zeta_{\perp,z} = s_{\perp,z}^{(2)} - \varepsilon (s_{\perp,z}^{(1)})^2.$$

Besides, for the substrates with a triangular lattice ($z_2 = 3$) there are also nondiagonal on $\dot{w}_i \dot{w}_j$ terms in (8) with

$$\Delta I_{ij} = -\frac{z_2^2 d^4}{m} \zeta_{\perp} K_0 K_2 \begin{pmatrix} 2w_y w_z & 2w_x w_z & 2w_x w_y \\ 2w_x w_z & -2w_y w_z & w_x^2 - w_y^2 \\ 2w_x w_y & w_x^2 - w_y^2 & 0 \end{pmatrix}.$$

By virtue of positive definiteness of the form (8) the coefficients $\Delta I_{\perp,z} > 0$. As a result, TRI leads to an increase in impurity main moments of inertia, that is the molecule becomes effectively heavier.

We have calculated the renormalized parameters for a number of atomic-molecular systems using for the impurity-matrix as well as for the impurity-substrate interactions the Lennard-Jones model with the

parameters corresponding to the gaseous phase [10]. It has been found that at real values of d/R_i the maximal relative change in moment of inertia is about 30%, and the renormalization of the crystal field amplitude may be as much as 50–60 %. Certainly, the estimations are quite rough because the Lennard-Jones potential is known to be extremely sensitive to a choice of its parameters. On the other hand, the real values of these parameters for a 2D system can differ significantly from those in the gaseous phase [3]. Nevertheless, it is clear that the properties of the system under consideration can be substantially affected by TRI, so that the renormalization effects due to TRI should be properly taken into account when discussing the physical phenomena in real systems.

4. Rotational heat capacity

Now we consider the rotational heat capacity of the dilute solution of diatomic molecules in a 2D atomic matrix. We restrict ourselves to the case of strong binding, when the molecules make small librations near their equilibrium positions normal to the layer plane. The impurity contribution to the free energy (per one impurity molecule) from the rotational degrees of freedom and the molecular in-plane translational motion has the form:

$$\Delta \mathcal{F} = \frac{\hbar}{\pi} \lim_{\delta \rightarrow 0} \int_0^{\infty} d\omega \coth \frac{\hbar\omega}{2T} \arctan \left(\frac{P(\omega, \delta)}{R(\omega)} \right).$$

Here

$$P(\omega, \delta) = 2\omega\delta [1 - \varepsilon\rho(\omega)(2\omega^2 - \omega_0^2)] - \mu(\omega)[\varepsilon\omega^2(\omega^2 - \omega_0^2) + a],$$

$$R(\omega) = (\omega^2 - \omega_0^2)[1 - \varepsilon\omega^2\rho(\omega)] - a\rho(\omega),$$

$$\rho(\omega) + i\mu(\omega) = \frac{1}{2N} \sum_{\mathbf{k}, \alpha=l,t} \frac{1}{(\omega + i\delta)^2 - \Omega_{\alpha}^2(\mathbf{k})},$$

ω_0 is the librational frequency of the rotator with nonrenormalized parameters (in the absence of TRI), $a = 2z_2^2 d^4 K_0^2 B / (m\hbar^2)$ is a parameter describing the TRI intensity.

For most real systems the librational frequency ω_0 is small as compared to the top edge Ω_{max} of the continuous spectrum of the pure 2D crystal, so that ω_0 is either in the gap ($\omega_0 < \Delta$) or in the continuous spectrum near its bottom. On the other hand, the less ω_0 and the lower temperature the easier to extract the rotational part from the total heat capacity containing also contributions from translational excitations (both from the continuous spectrum, and the local and

quasi-local states). Hereafter we consider the case of small ω_0 .

We start with $\omega_0 < \Delta$. For the light impurity ($\varepsilon > 0$) the local and quasilocal translational levels are close to Ω_{\max} , and their influence on low-temperature thermodynamics is negligible. Thus, the main contribution to the thermodynamic functions is from the rotational degrees of freedom. The rotational free energy and the heat capacity (per one particle) have the form:

$$\begin{aligned}\Delta\mathcal{F}_{\text{rot}} &= 2T \ln \left(2 \sinh \frac{\hbar\tilde{\omega}_0}{2T} \right), \\ \Delta C &= 2 \left(\frac{\hbar\tilde{\omega}_0}{2T} \sinh^{-1} \frac{\hbar\tilde{\omega}_0}{2T} \right)^2, \\ \tilde{\omega}_0^2 &= \omega_0^2 [1 - a\zeta_{\perp}] - as_{\perp}^{(1)},\end{aligned}\quad (9)$$

where $\tilde{\omega}_0$ is the librational frequency renormalized due to TRI. The result (9) corresponds to the heat capacity of a two-dimensional Einstein oscillator with the frequency $\tilde{\omega}_0$. As it should be, renormalization of the rotator motion parameters leads to an effective decrease of ω_0 and, hence, to an increase of a relative contribution from the rotational degrees of freedom to the low-temperature heat capacity.

In the case of the heavy impurity ($\varepsilon < 0$) the local level falls within the gap ($\omega_{\text{loc}} < \Delta$), and a contribution from ω_{loc} to thermodynamic functions can be comparable with that from the rotational degrees of freedom. Thus, the main contribution to the free energy and heat capacity from the impurity subsystem consists of two terms of the form (9) with frequencies $\tilde{\omega}_0$ and $\tilde{\omega}_{\text{loc}}$, being determined as two least roots of the equation $R(\omega) = 0$. Namely,

$$\begin{aligned}\tilde{\omega}_0^2 &= \omega_0^2 [1 - af(\omega_0, \omega_{\text{loc}})] - as_{\perp}^{(1)}, \\ \tilde{\omega}_{\text{loc}}^2 &= \omega_{\text{loc}}^2 [1 + af(\omega_0, \omega_{\text{loc}})], \\ f(\omega_0, \omega_{\text{loc}}) &= \frac{s_{\perp}^{(1)} + \omega_{\text{loc}}^2 s_{\perp}^{(2)}}{\omega_{\text{loc}}^2 - \omega_0^2}.\end{aligned}$$

If the spacing between the frequencies ω_{loc} and ω_0 is large in comparison with the TRI intensity, $a \ll (\omega_{\text{loc}}^2 - \omega_0^2)^2$, the considered excitations can be classified as librational and local ones with renormalized frequencies. In the opposite case, when $a \geq (\omega_{\text{loc}}^2 - \omega_0^2)^2$, «mixing» of the frequencies occurs, and, as a result, molecular librations and local oscillations are no longer well determined eigenstates.

The situation is more complicated, when the librational frequency is inside the continuous phonon spectrum near its bottom ($\omega_0 > \Delta$) [2,11]. Since for the heavy impurity $\omega_{\text{loc}} < \Delta$, the contribution to the

thermodynamic functions from the local excitations prevails over the contribution from the rotational degrees of freedom. Thus, the solutions with light impurities ($\varepsilon > 0$) are of main interest here. In this case the rotational free energy can be written as

$$\Delta\mathcal{F} = \frac{2T}{\pi} \int_{\Delta}^{\Omega_{\max}} d\omega \ln 2 \sinh \left(\frac{\hbar\omega}{2T} \right) \frac{\gamma_0}{(\omega - \tilde{\omega}_0)^2 + \gamma_0^2}, \quad (10)$$

where $\gamma_0 = -a\mu(\tilde{\omega}_0)/(2\tilde{\omega}_0)$ is a Lorentz peak half-width and $\tilde{\omega}_0$ is the same as in Eq. (9). It should be noted, that the validity of Eq. (10) is restricted to the condition $\omega_0 - \Delta \gg \gamma_0$, (i.e. ω_0 is not too close to the bottom of the continuous spectrum). Taking into account smallness of γ_0 , the rotational heat capacity can be approximately represented in the form (9). Thus, the rotational heat capacity at low temperatures has an exponential form

$$\Delta C = 2 \left(\frac{\hbar\tilde{\omega}_0}{T} \right)^2 \exp \left(-\frac{\hbar\tilde{\omega}_0}{T} \right), \quad (11)$$

unlike three-dimensional systems where the power-type dependence takes place [2]. Such a result is due to the gap in the phonon spectrum of the 2D monoatomic crystal commensurate with the substrate [3,12]. In this connection we remind that the matrix heat capacity also has an exponential form [3,12]

$$C_{\text{ph}} \sim \frac{\hbar\Delta}{T} \exp \left(-\frac{\hbar\Delta}{T} \right),$$

but its temperature dependence differs by preexponential factor from Eq. (11). This circumstance can be useful when extracting the rotational part from a measured total heat capacity particularly if ω_0 and Δ are close in magnitude.

5. Conclusion

The most pronounced effect resulting from the interaction between translational and rotational degrees of freedom consists in the radical change of the inertial properties of the impurity molecule. This manifests itself in the change in the form of the rotational kinetic energy operator as compared to the corresponding expression for the free rotator. The inertia tensor components become functions of molecular orientation, and the molecule, in terms of rotational motion, transforms into a «parametric rotor» whose effective kinetic energy is represented as a generalized quadratic form of the angular velocity components with a symmetry corresponding to the external crystal field. For example, if the substrate atoms form honeycomb structure, then within the present approximation the tensor of inertia remains diagonal, while it

has also nondiagonal components for substrates with triangular lattices.

The TRI also results in the renormalization of the crystal field parameters. However, although the corresponding corrections are sufficiently large, the potential form determined by the symmetry of the system remains unchanged.

We would like to note that the dynamics of a diatomic impurity in a 2D monoatomic matrix on a substrate is more complicated than in a 3D matrix of cubic symmetry [2,5]. Indeed, due to the high symmetry of the surroundings in 3D systems, TRI leads only to an increase in the molecular momentum of inertia without changing the form of the kinetic energy operator.

In view of possible experiments on the rotational heat capacity of 2D solid solutions of diatomic molecules in monoatomic matrices on commensurate substrates, the 2D solutions with light impurities are expected to be more preferable, because at low temperatures the contribution from the rotational degrees of freedom dominates over the contribution from the local translational excitations. Being richer from the theoretical standpoint, the systems with heavy impurities are more complicated for an experimental re-

search due to the problem of correct separation of contributions from the local and rotational excitations.

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