

## Heat capacity of 2D solid solution of diatomic molecules in rare gas matrix

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*Translational-rotational interaction in two-dimensional dilute solid solutions of diatomic molecular impurities in monoatomic cryomatrices is investigated theoretically. The interaction is shown to affect sufficiently the impurity rotational spectrum which in turn gives rise to low-temperature anomalies in the heat capacity. Peculiarities of the spectrum and the impurity contribution to the heat capacity are analyzed in details.*

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### 1. INTRODUCTION

Interaction between translational and rotational degrees of freedom in molecular crystals and solid solutions containing diatomic molecular impurities is one of the most essential factors determining their physical properties.<sup>1</sup> In particular, low-energy rotational excitations are responsible for anomalies in the low-temperature heat capacity. The character of these anomalies is uniquely determined by dynamic properties of an impurity-rotator, which, in turn, significantly depend on the translational-rotational interaction (TRI). Thus, low-temperature heat capacity measurements can be of use as an effective tool for the study of TRI. It is interesting to note that only inclusion of these effects made it possible to describe quantitatively<sup>2</sup> the experimental data on the heat capacity of three-dimensional Ar(Kr)-N<sub>2</sub>(O<sub>2</sub>) solutions.<sup>3</sup>

In two-dimensional (2D) atomic-molecular cryosolutions the TRI problem is of special interest because molecules move in the low symmetry crystal field, whose amplitude can vary in a rather wide range depending on monolayer and substrate materials. The effect of TRI on the dynamics of a diatomic substitutional impurity in a 2D monoatomic matrix adsorbed on a substrate has been investigated extensively in Refs. 4, 5. It was found,

that the TRI results in a drastic change of inertial properties of the impurity molecule. Mathematically it is expressed in the change of the rotational kinetic energy operator as compared to the corresponding expression for the free rotator. Peculiarities of the impurity dynamics manifest themselves in the temperature behavior of the heat capacity, that is in principle available for the experimental observation.

The aim of the present work is to investigate theoretically the effect of the TRI on the heat capacity due to rotational degrees of freedom in a dilute solution of diatomic molecules in monoatomic matrix commensurate with the substrate.

## 2. HAMILTONIAN AND ROTATIONAL SPECTRUM

We start with the Hamiltonian<sup>5</sup> obtained within a canonical-transformation method. Measuring energy parameters in units of the rotational constant  $B$  we can represent the Hamiltonian as

$$H = (1 - t_1)\hat{\mathbf{L}}^2 - t_2 \frac{\partial^2}{\partial \varphi^2} + t_3 \hat{\mathcal{M}} - p_1 x^2 + p_2 x^4. \quad (1)$$

Here  $\hat{\mathbf{L}}^2$  is a square of the angular momentum operator, equal to

$$\hat{\mathbf{L}}^2 = -\frac{\partial}{\partial x}(1 - x^2) \frac{\partial}{\partial x} - \frac{1}{1 - x^2} \frac{\partial^2}{\partial \varphi^2}, \quad x = \cos \vartheta, \quad (2)$$

$$\hat{\mathcal{M}} = x^2(x^2 - 1)^2 \frac{\partial^2}{\partial x^2} + 2x(x^2 - 1)(3x^2 - 1) \frac{\partial}{\partial x}, \quad (3)$$

$\vartheta$  and  $\varphi$  are azimuth and polar angles specifying the molecular axis orientation,  $p_1$  and  $p_2$  are renormalized crystal field parameters. The terms proportional to  $t_i$  ( $i = 1, 2, 3$ ) are caused by the renormalization of the rotational kinetic energy due to TRI. The quantities  $p_1$ ,  $p_2$  and  $t_i$  are determined by interparticle interactions and depend on the system parameters. Analysis shows that they satisfy the inequalities:  $p_1 > p_2$ ;  $0 < t_2 < t_1 < 1$ , and  $|t_3| < 1$ .

Wave functions of Schrödinger equation with the Hamiltonian (1) can be represented as an expansion in the normalized spherical harmonics  $Y_{lm}(\vartheta, \varphi)$ . Since the Hamiltonian (1) is axially symmetric, the magnetic quantum number  $m$  retains its meaning. The set of the wave functions can be grouped as even ( $g$ ) and odd ( $u$ ) relatively to inversion through origin. Rotational states with  $m = 0$  are nondegenerate, whereas the states with  $m \neq 0$  are doubly degenerate. It is also obvious, that the second term in (1), proportional to  $t_2$ , does not modify the levels with  $m = 0$ . Due to the complexity of the

Hamiltonian (1), in general case impurity rotational levels can be calculated only numerically.

To investigate quantitatively the effect of TRI on the dynamics and thermodynamics of real systems it needs to be known the magnitudes of  $p_1$ ,  $p_2$  and  $t_i$ . It is difficult to determine unambiguously these values because neither an explicit form of the interparticle potential nor values for its parameters are in fact known. However, qualitative conclusions concerning effects we are interested in can be made if we use reasonable estimates for the ratios between these parameters.

In Refs. 5, 6 the rotational spectrum of the impurity molecule as a function of parameter  $p = p_1 - 2p_2$  was calculated numerically with<sup>5</sup> and without<sup>6</sup> regard to TRI. A ratio  $p_2/p_1$  was chosen to be 1/8, which corresponds to that in real systems. It turned out that as  $|p|$  increases the low-lying levels approach each other in pairs:  $A_1^g, A_1^u$  at  $p > 0$  and  $A_1^g, E_1^u$  at  $p < 0$ . TRI was found to make this effect more pronounced.<sup>5</sup> These are the features of the spectrum that are responsible for anomalies in the low-temperature heat capacity. Such effects arise in the temperature region where the basic contribution to the heat capacity is from a few low-lying levels.

The reason why the levels can approach closely at large  $|p|$  becomes clear from the following considerations. Let us begin with  $p_1 < 0$ ,  $|p_1| \gg 1$ . In this case a molecule in the matrix behaves like a near-planar rotator. Let  $\vartheta = \pi/2 + \gamma$ , where  $\gamma \ll 1$ . Then in the basic approximation with respect to a small parameter  $\gamma$  the Hamiltonian (1) can be written as

$$H = H_1 + H_2, \quad (4)$$

where the Hamiltonian  $H_1$  describes a harmonic oscillator

$$H_1 = -(1 - t_1) \frac{\partial^2}{\partial \gamma^2} + |p_1| \gamma^2 \quad (5)$$

and  $H_2$  describes a free planar rotator

$$H_2 = -(1 - t_1 + t_2) \frac{\partial^2}{\partial \varphi^2}, \quad (6)$$

From (4)-(6) follows, that in Schrödinger equation variables can be divided up and the rotator wave function  $\Psi_{n,m}$  has a form:

$$\Psi_{n,m}(\gamma, \varphi) = \frac{1}{\sqrt{2\pi}} \psi_n(\gamma) \exp(im\varphi), \quad n = 0, 1, \dots; \quad m = 0, \pm 1, \dots$$

where  $\psi_n(\gamma)$  is a harmonic oscillator wave function. The corresponding eigenvalues can be written as

$$E_{n,m} = \sqrt{4p_1(1 - t_1)} \left( n + \frac{1}{2} \right) + (1 - t_1 + t_2)m^2, \quad (7)$$

Levels  $E_{0,0}$  and  $E_{0,1}$  correspond to the ground state  $A_1^g$  and first excited state  $E_1^u$ , respectively. The difference between them is equal to

$$E_{0,1} - E_{0,0} = 1 - t_1 + t_2. \quad (8)$$

Since  $0 < t_2 < t_1$ , the TRI causes these two levels draw closer together. As a result, the anomalies of the thermodynamic functions become more pronounced.

We proceed now to positive  $p$ . In the limit  $\alpha = p/(1-t_1) \gg 1$ , eigenfunctions  $\psi$  of the Hamiltonian (1) corresponding to low-lying levels are located near  $x = \pm 1$ . It allows us to neglect the terms proportional to  $t_2$  and  $t_3$  in the Hamiltonian (1). Then, dividing variables  $x$  and  $\varphi$  in the Schrödinger equation, for the  $x$ -depending part of the wave function we obtain

$$\frac{d}{dx}(1-x^2)\frac{d}{dx}\psi_{n,m}(x) + \left(\lambda_{n,m} - \alpha(1-x^2) - \frac{m^2}{1-x^2}\right)\psi_{n,m}(x) = 0, \quad (9)$$

where  $\lambda_{n,m} = \alpha + E_{n,m}/(1-t_1)$ . Equation (9) coincides with the equation for the oblate spheroidal harmonics. Using the asymptotics of the spectrum  $\lambda_{n,m}$ <sup>7</sup> one can show, that the difference  $\Delta E$  between the ground ( $A_1^g$ ) and the first excited ( $A_1^u$ ) levels is equal to

$$\Delta E = 32\alpha \exp(-2\sqrt{\alpha}).$$

Note, that at large  $|p|$ , irrespective of the sign of  $p$ , the term proportional to  $t_3$  results only in small shifts of low-lying energy levels. Thus, it is the term proportional to the parameter  $t_1$  that has marked effect on the low-lying levels of the molecular rotational spectrum and consequently on the thermodynamics of 2D solid solutions. Hence, while studying the low-temperature behavior of the heat capacity considerable attention will be given to the effects which are caused by this term. Since  $t_1 > 0$ , it means that due to TRI an impurity molecule become effectively heavier.

The TRI effect on two lowest levels, caused by the first term in (1) is shown on Fig.1a (for  $p < 0$ ) and Fig. 1b (for  $p > 0$ ). As can be seen, owing to TRI the two levels begin to approach each other at smaller values of  $|p|$ .

### 3. HEAT CAPACITY

Evaluating eigenenergies, we can easily calculate the impurity contribution due to rotational degrees of freedom to the thermodynamic functions of a 2D dilute solid solution. The partition function  $Z$  of the rotational subsystem has a form (per one impurity):

$$Z = w_g Z_g + w_u Z_u, \quad Z_{g(u)} = \sum g_i \exp[-E_i^{g(u)}/T], \quad (10)$$

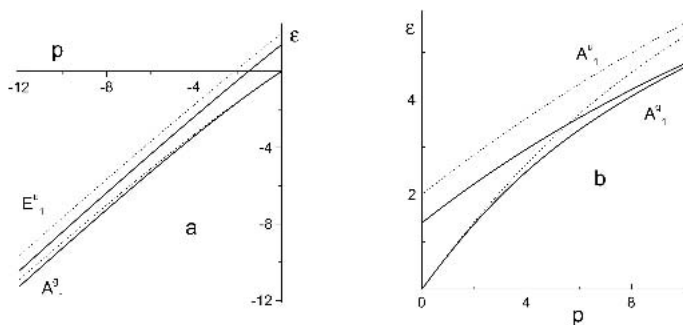


Fig. 1. Two lowest levels of the impurity rotational spectrum with (solid lines,  $t_1 = 0.3$ ) and without (dotted lines) regard to TRI:  $p < 0$  (a);  $p > 0$  (b).

where  $g_i$  is the degeneracy of the level  $E_i$ . Here the fact, that even and odd states have different nuclear degeneracy ( $w_g$  and  $w_u$ ), is taken into account. Summation in (10) is made over either even or odd levels. The rotational heat capacity per one molecule is

$$C = \frac{\partial}{\partial T} T^2 \frac{\partial}{\partial T} \ln Z.$$

The values for the weights  $w_g$  and  $w_u$  depend on whether the nuclei spin is integer or half-integer. When, for example, nitrogen molecules are chosen as impurities the weights are

$$w_g = 2/3, \quad w_u = 1/3 \quad \text{for } {}^{14}\text{N}_2; \quad (11)$$

$$w_g = 1/4, \quad w_u = 3/4 \quad \text{for } {}^{15}\text{N}_2. \quad (12)$$

Comparing (11) and (12), we see that for solutions containing  ${}^{15}\text{N}_2$  molecules the contribution to the impurity heat capacity from odd states is dominant. The rotational constant  $B$  equals 2.875 K for  ${}^{14}\text{N}_2$  and 2.684 K for  ${}^{15}\text{N}_2$ .<sup>8</sup>

As expected, for both isotope modifications of nitrogen molecules the effect is more pronounced at positive values of crystal field parameters. Fig. 2 illustrates the TRI influence caused by the first term in (1) on the rotational heat capacity at  $p = 4.5$ .

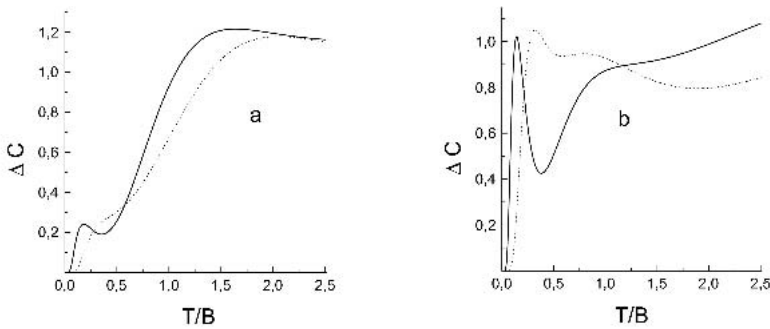


Fig. 2. Heat capacity of a 2D solid solution of  $^{14}\text{N}_2$  (a), and  $^{15}\text{N}_2$  (b) in a rare gas matrix with (solid lines,  $t_1 = 0.3$ ) and without (dotted lines) regard to TRI.

#### 4. CONCLUSION

The TRI has a profound effect on the thermodynamic properties of the impurity subsystem of 2D solutions. It manifests itself as appearance of a well-marked low temperature peak on the temperature dependence of the rotational heat capacity. The predicted behavior of  $C(T)$  is in principle available for experimental observation.

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