

## ROTATIONAL STATES OF COUPLED SPHERICAL MOLECULES

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The method of calculation is shown with respect to rotational energy levels and rotational eigenstates in one of two rotating spherical molecules coupled with orientational potentials. This method is applied to tetrahedral molecules dispersed in rare gas matrix. The comparison with experimental results by neutron inelastic scattering gives the most suitable strength and symmetry of the potential between two rotators.

In solid phase or in rare gas matrix, the spherical molecule like a type of tetrahedral  $AX_4$  or octahedral  $AX_6$  has quite large degree of freedom of rotational motion even in lower temperature such as liquid-helium temperature. Due to the interaction with the surrounding molecules and with the neighboring coupled spherical molecule, each of two molecules has a hindrance in rotational motion. As the anisotropic potential becomes greater, it changes gradually from nearly free rotation to considerably hindered rotation. When the potential is much stronger than the thermal energy, the so-called rotational tunneling appears by the symmetrical equivalence. The structure of splitting in the energy levels of tunneling system is characterized by the type of site symmetry.

The rotational Hamiltonian of one hindered molecule is given by

$$H^{(1)}(\omega) = K + A \cdot u_{\tau}(\omega) + V(\omega) \quad , \quad (1)$$

where  $K$  is the kinetic energy and  $V(\omega)$  the octahedral crystalline field which is a function of the Euler angles  $\{\omega\}$  of the molecule in site. The 3rd order of tetrahedral function  $u_{\tau}(\omega)$  ( $\tau=1\sim 7$ ) should be zero in the case of octahedral unit because of higher symmetry. When the field strength  $A$  increases, the energy levels tend to make groups and the rotational states approach tunneling motion. In octahedral case, there are four types:  $T_d$ ,  $D_{2d}$ ,  $C_{3v}$ , and  $C_{2v}$  while there is one type in tetrahedral case.

Next, we proceed to the system of two molecules which orientationally interacts directly with each other and which are surrounded by other molecules. We may introduce the Hamiltonian of such a system in the following:

$$H = H^{(1)}(\omega_1) + H^{(1)}(\omega_2) + \sum_{\tau, \nu} C_{\tau\nu} u_{\tau}(\omega_1) u_{\nu}(\omega_2). \quad (2)$$

Here,  $\omega_1$  or  $\omega_2$  is the Euler angles in molecule 1 or 2, and the coefficient  $C_{\tau\nu}$  is offered by octopole-octopole interaction. Now, we use the above relation for the tetrahedral molecules. Moreover, we take up only the terms  $\tau = \nu = 1$  because it is too complicated to compute as the beginning step. By comparison with the experimental results,<sup>1)</sup> it is concluded that the (1,1) component gives rise to the rather strong field using the normal value of octopole moments. A typical potential map is shown in Fig.1. Each molecule rotates by z-axis from  $T_d$  orientation and the connection line runs along (111) direction.

Before we examine the contribution of other components in the interaction, it is necessary to check the behavior in molecular-field approximation. If the Euler angles  $\omega_2$  are averaged, Hamiltonian for two-particles are shown as

$$\langle H \rangle_2 = H^{(1)}(\omega_1) + E_2 + c_1 \cdot u_1(\omega_1), \quad (3)$$

where the constant is

$$c_1 = C_{11} \langle u_1(\omega_2) \rangle_2. \quad (4)$$

Basically, Hamiltonian with the averaged potential corresponds to the single-particle Hamiltonian  $H^{(1)}(\omega)$ . But, it is important to investigate the self-consistency in Equations (3) and (4) because we employ the averaged Hamiltonian in (3) in order to calculate the averaging over  $u_1$  in (4).

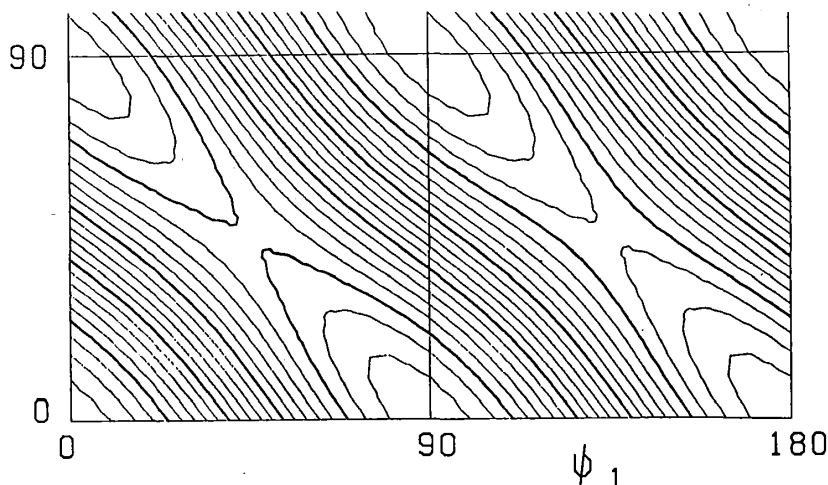


Fig.1

1) B. Asmussen, W. Press, M. Prager, and H. Blank, *J. Chem. Phys.* **98**, 158 (1993).