

NONRIGID MOLECULES WITH SEVERAL LARGE-AMPLITUDE COORDINATES

B.I.Zhilinskii

Department of Chemistry, Moscow State University, Moscow 117 234 USSR

ABSTRACT

The vibration-rotation problem of inorganic molecules composed of a rigid core and one or two atoms which display almost free motion around this core is discussed. Such molecules as LiCN, LiBH₄, TlNO₃, LiBO₂, ArN₂, K₂SO₄ are appropriate examples. The nonempirical method is proposed which uses the ab initio potential surface and treats two internal coordinates as corresponding to large-amplitude ones. The variational method is used to calculate the vibration-rotation energy levels and wavefunctions. Some features of the microwave spectrum of nonrigid inorganic molecules is qualitatively explained on the basis of simple semiempirical method, using the topological structure of the potential surface.

INTRODUCTION

Inorganic chemistry provides a number of molecules which cannot be properly described by a well-known rigid model. The nonrigid (ref. 1) or semirigid models (refs. 2,3) must be applied to calculate the structure and the vibration-rotation spectra of such molecules. Only one type of nonrigid molecules with several large-amplitude coordinates will be discussed here. These are the molecules composed of a rigid core and one or two atoms which move almost freely around this core. Such molecules as LiCN, LiBO₂, LiBH₄, K₂SO₄, TlNO₃ are appropriate examples (ref. 4). To obtain good quantitative description of the vibration-rotation spectra the nonempirical variational method is proposed which is applicable to simple triatomic molecules with known potential surface. To explain the qualitative features of the vibration-rotation spectra for more complex molecules such as LiBH₄, TlNO₃, K₂SO₄ the simple semiempirical method is proposed which uses only the topological structure of the potential surface for large-amplitude motion.

QUANTITATIVE METHOD

We develop the variational method for calculation the vibration-rotation levels of a triatomic system with a diatomic rigid core. We suppose first the fulfillment of the adiabatic approximation then separate the center of mass of the system and introduce a body-fixed frame, connected only with the diatomic fragment (ref. 5). The location of the atom with respect to the diatomic core is characterized by two large-amplitude coordinates, r, θ (Fig. 1). To construct the effective nonrigid Hamiltonian with two internal degrees of freedom we average the total Hamiltonian with the vibrational function depending on R . The resulting Hamiltonian depends on r and θ as well as on the external variables $\varphi_1, \theta_1, \varphi$

$$H = -\frac{1}{2\mu_2} \Delta_{\vec{r}} + \frac{1}{2\mu_1 R_0^2} (J^2 + L^2) \quad (1)$$

$$- \frac{1}{2\mu_1 R_0^2} (2L_z^2 + L_+ J_- + L_- J_+) + V(r, \theta);$$

$$\frac{1}{\mu_1} = \frac{1}{m_a} + \frac{1}{m_b} \quad ; \quad \frac{1}{\mu_2} = \frac{1}{m_c} + \frac{1}{m_a + m_b} .$$

Here $L_{\pm} = L_x \pm iL_y$, L_x, L_y, L_z are components of the angular momentum operator for the particle associated with vector \vec{r} , P is a momentum operator for the particle associated with vector \vec{R} . The operators L and P are identified in the body-fixed system. J is the total orbital angular momentum for the three particle problem. $V(r, \theta)$ is the potential integrated over the R -dependent vibrational function. R_0 is some effective value of R .

We construct the basis for the variational calculation by prelimi-

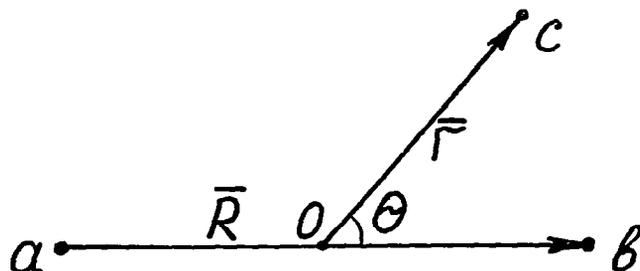


Fig. 1. Coordinates for triatomic molecule of the LINC type. The point O is situated in the center of mass of the rigid core.

nary crude separation of variables in the Hamiltonian (1). In the first step we introduce two auxiliary Hamiltonians H_r and H_θ

$$H_r = -\frac{1}{2\mu_2 r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V_r(r); \quad (2)$$

$$H_\theta = \frac{1}{2\mu_1 R_0^2} J^2 + \left(\frac{1}{2\mu_1 R_0^2} + \frac{1}{2\mu_2 r_0^2} \right) L^2 - \frac{1}{2\mu_1 R_0^2} \left(2L_z^2 + L_+ J_- + L_- J_+ \right) + V_\theta(\theta). \quad (3)$$

The motion over the r variable is supposed to be close to r_0 , while $V_r(r)$ and $V_\theta(\theta)$ are effective potentials obtained in some way from the total potential.

The multiplication of the eigenfunctions of the operators (2) and (3) provides the basis for the calculation of the eigenvalues of operator (1). This basis gives the possibility of analytical evaluation of all matrix elements. The approach described above was used for vibration-rotation level calculation of the LiCN and KCN molecules. The results of such model calculations are now published in J.Mol.Spectrosc. (ref. 5). So I shall further discuss the semi-empirical qualitative method.

QUALITATIVE METHOD

Consider such ionic molecules as LiBH_4 , TlNO_3 , InInCl_4 , K_2SO_4 etc. The important peculiarity of these molecules is the existence of several equilibrium equivalent sites of external atom with respect to the rigid core. Moreover the external atom possesses large-amplitude motion whereas the rigid core possesses only the small vibrations. Quantum mechanical calculations (ref. 6,7), spectroscopic (ref. 8) and electron diffraction data (ref. 4) confirm this statement.

Let ABX_4 be the molecule with the rigid tetrahedral core BX_4 . The potential surface for the atom A motion around BX_4 core qualitatively may be described, for example, as follows. The location of atom A over the center of the side corresponds to the minimum of the potential energy surface. The locations of atom A over the apices of the tetrahedron and over the middle of the edges correspond respectively to the maxima and the saddle points of the potential

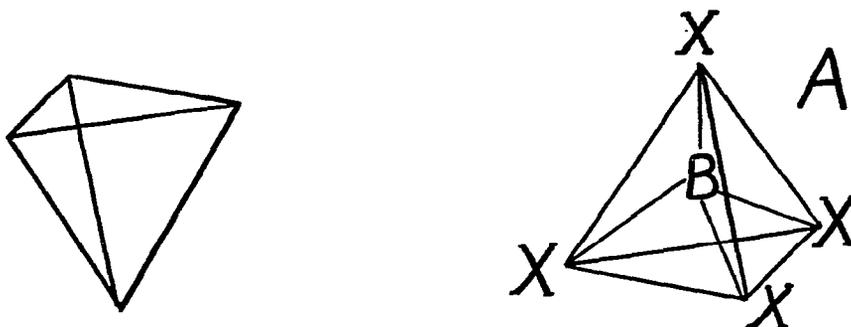


Fig. 2. One-dimensional graph representing the potential energy surface for the atom A motion around the rigid BX_4 tetrahedron in the ABX_4 type molecules.

energy surface. Such structure of the potential energy surface is obtained for the $LiBH_4$ molecule (ref. 6). A simple one-dimensional graph may be used as a model for such potential surface. The vertices of this graph correspond to the minima of the potential and the edges connect those vertices between which there is a saddle point (Fig. 2). Now we introduce the effective Hamiltonian H_{eff} which describes the motion of a particle in the one-dimensional graph. To obtain the eigenfunctions and eigenvalues of this effective Hamiltonian we use the variational method with the trial functions corresponding to the states localised in the minima. Thus for ABX_4 molecule we have four functions and two types of matrix elements

$$\langle \psi_i | H_{eff} | \psi_j \rangle = \beta, \quad i \neq j.$$

$$\langle \psi_i | H_{eff} | \psi_i \rangle = \alpha.$$

The solution of a simple secular equation

$$\det \begin{pmatrix} \alpha - E & \beta & \beta & \beta \\ \beta & \alpha - E & \beta & \beta \\ \beta & \beta & \alpha - E & \beta \\ \beta & \beta & \beta & \alpha - E \end{pmatrix} = 0$$

yields the energy levels

$$E_{1,2,3} = \alpha - \beta,$$

$$E_4 = \alpha + 3\beta.$$

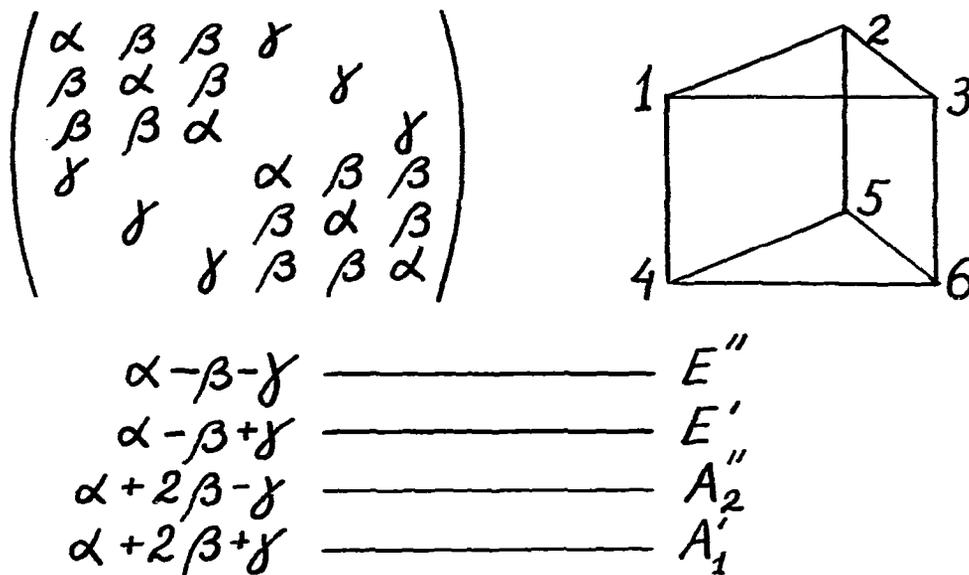


Fig. 3. One-dimensional graph, matrix form of the Hamiltonian and the energy splitting for the M atom motion around NX_3 rigid core in the MNX_3 type molecules. The energy levels are labelled according to the irreducible representations of the symmetry group of the rigid core $/D_{3h}/$.

We can simplify the problem using the symmetry arguments. If the functions ψ_i transform according to the irreducible representation A_1 of the local symmetry group C_{3v} the resulting molecular functions transform as $A_1 + F_2$ irreducible representations of T_d group. The type of energy level splitting due to the large-amplitude motion is fully described by the topological structure of the molecular graph mentioned above /i.e. by the parameter β under the assumptions of the simple molecular orbital theory/. The same technique may be successfully applied to other molecules. We present here the energy level splitting for MNX_3 type molecules (Fig. 3). In this case three different matrix elements are to be used.

If the molecule consists of two atoms and a rigid core, as in the case of K_2SO_4 , six functions ψ_{12} , ψ_{13} , ψ_{14} , ψ_{23} , ψ_{24} , ψ_{34} , are to be used. The function ψ_{ij} describes the two-particle state with the particles localized in the minima i and j . For example we have the following energy levels for two particles in the one-dimensional tetrahedral graph /the model for K_2SO_4 molecule/.

$$E_1 = 2\alpha + 4\beta,$$

$$E_{2,3,4} = 2\alpha,$$

$$E_{5,6} = 2\alpha - 2\beta.$$

In this case we can construct the wavefunctions with proper spatial and permutational symmetry. The quantitative evaluation of the parameter β strictly depends on the magnitude and the shape of the potential, and thus we cannot predict any reliable values.

ACKNOWLEDGEMENTS

I am very grateful to Dr.P.R.Bunker who made it possible for me to use his results prior to publication.

REFERENCES

- 1 A.R.Hoy and P.R.Bunker, *J.Mol.Spectrosc.*, 52(1974)439.
- 2 A.Bauder, R.Meyer, and H.H.Günthard, *Mol.Phys.*, 28(1974)1305.
- 3 P.R.Bunker, private communication.
- 4 N.G.Rambidi, *J.Mol.Struct.*, 28(1975)77, 89.
- 5 V.A.Istomin, N.F.Stepanov, and B.I.Zhilinskii, *J.Mol.Spectrosc.*, in press.
- 6 A.I.Boldyrev, O.P.Charkin, N.G.Rambidi, and V.I.Avdeev, *Chem.Phys.Lett.*, 44(1976)20.
- 7 E.Clementi, H.Kistenmacher, and H.Popkie, *J.Chem.Phys.*, 58(1973) 2460.
- 8 P.Kuijpers, T.Törring, and A.Dymanus, *Chem.Phys.Lett.*, 42(1976) 423.