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VIBRATION–ROTATION HAMILTONIAN FOR NONRIGID TRIATOMIC MOLECULES WITH DIATOMIC RIGID CORE

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Several semi-rigid model hamiltonians are constructed for calculation of the vibration–rotation spectra of nonrigid triatomic molecules with diatomic rigid core. The models proposed are applicable to molecules with an elliptical nonrigid trajectory. This means that the potential energy surface corresponding to the interaction between the external atom and rigid core possesses minima close to elliptical surface. Such molecules as MCN (M = Li, Na, K) are appropriate examples.

1. Introduction

In recent years considerable interest has awoken in the investigations of nonrigid ionic or van der Waals molecules (see, for example, reviews [1,2]). The simplest molecules of this type are the triatomic molecules composed of a diatomic rigid core and an atom which can move almost freely around this core. MCN ionic molecules (M is an alkali metal atom) or van der Waals complexes (ArO_2, ArHCl, ArN_2) are appropriate examples.

In this paper we generalize the method proposed earlier [3–5] for the calculation of vibration–rotation levels for nonrigid triatomic molecules with diatomic rigid core. We have developed the elliptical model which enables us to treat the problem with a highly nonspherical potential for the external atom motion.

We must take into account the chemical structure of the molecules to make the proper choice of internal variables. It is known [6] that for LiCN type molecules almost free rotation of the cation takes place at rather high temperatures. If we suppose the LiCN molecule to be composed of ions (the so-called ionic model) we can indi-

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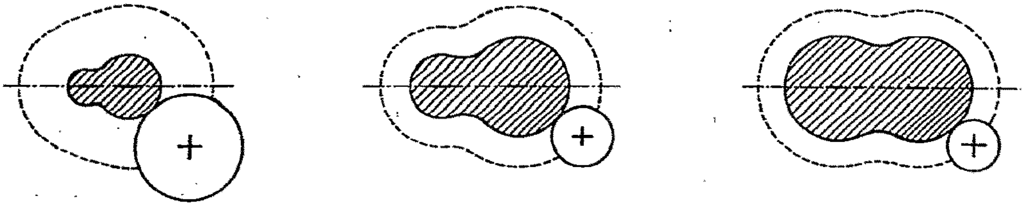

Fig. 1. Trajectories of nonrigid cation motion for different relative sizes of the ions.

cate the possible ways of the cation motion. This way will be called the nonrigid trajectory. The corresponding motion is the bending motion. Fig. 1 shows the possible ways of the cation depending on the size of the cation and anions. It can be seen that this trajectory may take the form of a slightly or strongly deformed ellipsoid and a slightly deformed sphere. The radial vibration of the cation seems to have a rather high frequency and small amplitude. For example, the Ismail data [7,8] show that the radial frequency for MCN molecules in an inert gas matrix is several times larger than the bending mode. So the ionic molecules have in essence only one large amplitude coordinate, but this coordinate is very complicated. The slightly bound van der Waals complexes surely possess two large-amplitude coordinates, bending and radial ones, but these coordinates are almost independent. The experimental data on the ArO_2 and ArN_2 molecules support this suggestion [9,11].

We have considered earlier the simplest model for a triatomic molecule with two large-amplitude coordinates [4]. To describe the position of the atom moving around the rigid diatomic core we used spherical coordinates which were supposed to be nonrigid ones. We call such model a spherical one. This model is well suited for the kinetic energy representation, but the potential energy may have a rather complicated form depending on the molecule. So the procedure developed in ref. [4] requires rather elaborated calculations in some cases due to the crude separation of nonrigid variables.

The purpose of the present article is to improve initial approximate hamiltonians which result in the construction of the basis for variational calculations. Here we propose a model adapted to the nonrigid trajectory of elliptical form. We investigate two possibilities. Firstly we use a change of variables which transforms the elliptical trajectory into a spherical one. In this case the kinetic energy operator may be written as the sum of the operator for the spherical case and some additional terms responsible for deviations of the real operator from the spherical one. Even in the case when the trajectory may differ from an elliptical one we propose to use the same change of variables, because such a procedure results in a rather simple form of the kinetic energy operator.

On the other side we can use elliptical coordinates. We have shown that in spite of the complicated form of the kinetic energy operator it is possible to construct some effective one-dimensional equations for the description of the vibration–rotation problem. In this paper we consider only triatomic molecules but the method proposed may be easily generalized to molecules composed of an atom possessing almost free motion around a linear rigid core (ArOCS is an appropriate example [12]). The generalization to the case of "nonlinear rigid core + atom" systems is also possible.

2. Total hamiltonian

The vibration–rotation hamiltonian for triatomic molecules in cartesian coordinates has the form

$$H = -\frac{1}{2m_a}\Delta_{\bar{r}_a} - \frac{1}{2m_b}\Delta_{\bar{r}_b} - \frac{1}{2m_c}\Delta_{\bar{r}_c} + V(|\bar{r}_i - \bar{r}_j|)\,, \tag{1}$$

where $\bar{r}_a$, $\bar{r}_b$, $\bar{r}_c$ are vectors characterizing the positions of the atoms in a laboratory fixed coordinate system. We assume that a and b form the rigid core and atom c moves around this core. We use Jacobi coordinates to separate the centre-of-mass motion (fig. 2):

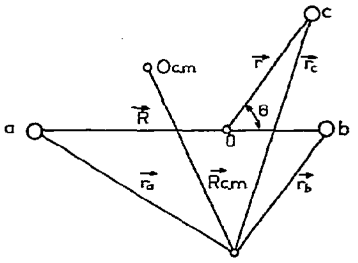

Fig. 2. Jacobi coordinates for a triatomic system.

$$\bar{R}_{\mathrm{c.m.}} = (m_a\bar{r}_a + m_b\bar{r}_b + m_c\bar{r}_c)/(m_a + m_b + m_c)\,, \tag{2}$$

$$\bar{R} = \bar{r}_b - \bar{r}_a\,, \quad \bar{r} = \bar{r}_c - (m_a\bar{r}_a + m_b\bar{r}_b)/(m_a + m_b)\,.$$

In Jacobi coordinates the hamiltonian (1) may be rewritten as

$$H = -\frac{1}{2M}\Delta_{\bar{R}_{\mathrm{c.m.}}} - \frac{1}{2\mu_1}\Delta_{\bar{R}} - \frac{1}{2\mu_2}\Delta_{\bar{r}} + V(\bar{R}, \bar{r})\,,$$

$$M = m_a + m_b + m_c\,, \quad \mu_1^{-1} = m_a^{-1} + m_b^{-1}\,, \quad \mu_2^{-1} = (m_a + m_b)^{-1} + m_c^{-1}\,. \tag{3}$$

Now we transform the hamiltonian to the molecule-fixed coordinate system. It is suitable to use the coordinate frame connected only with the rigid core and take the hamiltonian introduced earlier for diatomic molecules [13,14]

$$H = -\frac{1}{2\mu_1}\left(\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right) - \frac{1}{2\mu_2}\Delta_{\bar{r}} + \frac{1}{2\mu_1 R^2}[J^2 + L^2 - (2L_z^2 + L_+J_- + L_-J_+)] + V(R, r, \theta)\,. \tag{4}$$

Here L_x, L_y, L_z are the angular momentum operators for the particle associated with the vector $\bar{r}$, $L_\pm = L_x \pm iL_y$, J is the operator of the total angular momentum. The z-axis of the body fixed coordinate system aligns along the vector $\bar{R}$. $\bar{r}$ has the spherical coordinates, r, θ, ϕ in the body fixed system. The coordinates R, r, θ are the internal ones. Let us now average the hamiltonian (4) over the rigid variable R with the vibrational wavefunction. We obtain the effective operator, describing the nonrigid internal motion and the rotation of the system as a whole. This effective operator surely corresponds to some concrete vibrational state of the rigid core

$$H = -\frac{1}{2\mu_2}\Delta_{\bar{r}} + \frac{1}{2\mu_1 R_0^2}[J^2 + L^2 - (2L_z^2 + L_+J_- + L_-J_+)] + V(r, \theta)\,. \tag{5}$$

Here $V(r, \theta)$ is the potential $V(R, r, \theta)$ averaged over the variable R. R_0 is some effective value of R resulting from the averaging of $1/R^2$ with the vibrational wavefunction. The operator (5) is the initial one for the further use. When the potential can be represented in the form

$$V(r, \theta) = V_r(r) + V_\theta(\theta) + W(r, \theta)\,,$$

where $W(r, \theta)$ is small, the separation of variables in spherical coordinates is a rather good approximation. The resulting auxiliary operators

$$H_\theta = \frac{1}{2\mu_1 R_0^2}[J^2 - (2L_z^2 + L_+J_- + L_-J_+)] + \left(\frac{1}{2\mu_1 R_0^2} + \frac{1}{2\mu_2 r_0^2}\right)L^2 + V_\theta(\theta)\,, \tag{6}$$

$$H_r = -\tfrac{1}{2}\mu_2^{-1}\,\mathrm{d}^2/\mathrm{d}r^2 + V_r(r)\,, \tag{7}$$

are just the operators which were used in our previous publication [4] for the variational solution of the vibration rotation problem. But the algorithm proposed cannot be applied to the case with a large W-term and particularly to the case with a significantly elliptical nonrigid trajectory. So we shall try to modify the method used earlier adapting it to the special case of an elliptical potential. We suppose that the potential $V(r, \theta)$ possesses minima at every value of θ and the set of these minimum points form the elliptical surface which may be described as follows

$$x^2/b^2 + y^2/b^2 + z^2/a^2 = 1\,.$$

Then we do the change of variables which transforms the elliptical surface into a spherical one (see, for example, the problem from ref. [15])

$$x = (b/r_0)x'\,, \quad y = (b/r_0)y'\,, \quad z = (a/r_0)z'\,. \tag{8}$$

We have the equation for the sphere of the radius r_0 in new variables. We use now the same series expansion for the potential V as in the spherical model

$$V = V(r, \theta) = \sum_{k,m} C_{km}(r - r_0)^k \cos^m\theta \, . \tag{9}$$

It must be noted that for the most simple elliptical potential of the form $V = k(\lambda - \lambda_0)^2$, the transformed potential may be approximated as (see fig. 3)

$$V = k_1(r - r_0)^2 + k_2 \cos^2\theta (r - r_0)^2 + \ldots .$$

The second term is responsible for the interaction of radial and bending motions. It increases when the nonrigid trajectory becomes more elliptical. This limits surely the applicability of the method proposed to cases of slightly elliptical potential surfaces. But it is just the situation which takes place for LiCN type molecules.

We transform now the hamiltonian (5) to new variables

$$\Delta_{\bar{r}} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{r_0^2}{b^2} \Delta_{\bar{r}'} + \frac{r_0^2(b^2 - a^2)}{a^2 b^2} \frac{\partial^2}{\partial z'^2} \, , \tag{10}$$

or equivalently

$$\Delta_{\bar{r}} = \frac{r_0^2}{a^2} \Delta_{\bar{r}'} + \frac{r_0^2(a^2 - b^2)}{a^2 b^2} \left(\frac{\partial^2}{\partial x'^2} - \frac{\partial^2}{\partial y'^2} \right) . \tag{11}$$

One or another form of the operator may be more suited depending on the concrete model. Below we will never use primes for new variables and the change of variables will be denoted by an arrow (→).

The change of variables introduced above does not affect the operators $L_z, J^2, J_\pm$. To transform the operators $L_\pm$ and L^2 we define new operators $E_\pm$:

$$E_\pm = (\pm x + \mathrm{i}y)\partial/\partial z \, , \tag{12}$$

which are non-hermitian and obey the relation

$$(E_\pm)^+ = E_\mp \, . \tag{13}$$

Under the change of variables

$$E_\pm \to (b/a) E_\pm \, ,$$

and

$$L_\pm \to \frac{a}{b} L_\pm + \frac{a^2 - b^2}{ab} E_\pm \, , \tag{14}$$

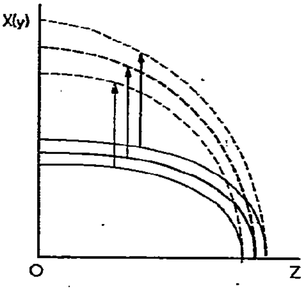

Fig. 3. Change of the potential shape under the scale transformation of variables (8).

$$L^2 = L_z^2 + \tfrac{1}{2}(L_+L_- + L_-L_+) \to \frac{a^2}{b^2}L^2 + \left(1 - \frac{a^2}{b^2}\right)L_z^2$$

$$+\frac{a^2 - b^2}{2b^2}(L_+E_- + E_+L_- + L_-E_+ + E_-L_+) + \tfrac{1}{2}\left(\frac{a^2 - b^2}{ab}\right)^2 (E_+E_- + E_-E_+) . \tag{15}$$

Taking into account relations (10), (14) and (15), the hamiltonian (5) may be written as

$$H = -\frac{1}{2\mu_2}\left[\frac{r_0^2}{b^2}\Delta_{\bar{r}} + \left(\frac{r_0^2}{a^2} - \frac{r_0^2}{b^2}\right)\frac{\partial^2}{\partial z^2}\right] + \frac{1}{2\mu_1 R_0^2}\left[J^2 + \frac{a^2}{b^2}L^2 + \left(1 - \frac{a^2}{b^2}\right)L_z^2\right.$$

$$+\frac{a^2 - b^2}{2b^2}(L_+E_- + L_-E_+ + E_-L_+ + E_+L_-) + \tfrac{1}{2}\left(\frac{a^2 - b^2}{ab}\right)^2(E_+E_- + E_-E_+) - 2L_z^2$$

$$\left. -\frac{a}{b}(L_+J_- + L_-J_+) - \frac{a^2 - b^2}{ab}(E_+J_- + E_-J_+)\right] + V(r, \theta) . \tag{16}$$

The hamiltonian (16) is obtained by using the body fixed coordinate frame connected only with the rigid core. It is more suited to connect the moving frame with the "nonrigid vector" $\bar{r}$ when the van der Waals molecules are considered. Another kind of the coordinate transformation is to be used in this case to take into account the elliptical character of the nonrigid trajectory. This problem is treated in appendix A. The disadvantage of the operator (16) is the coincidence of the center of mass of the rigid core and the center of the elliptical potential surface. For treating the isotopic substitution problem it is desirable to have the possibility of moving the center of the elliptical potential surface along the rigid core line. We consider the corresponding modifications in appendix B.

2.1. Bending-rotation and radial operators

We consider now the variational method of solving the eigenvalue problem for the operator (16). First of all we introduce the operators H_θ and H_r similar to operators (6) and (7). Surely operators (6) and (7) may be used as auxiliary operators for the hamiltonian (16) but in such a case the elliptical character of the transformed kinetic energy will be neglected. To reach a more accurate expression for the H_θ and H_r operators it is necessary to investigate the matrix elements $\langle nl'm'|A|nlm\rangle$, where n is the quantum number for the oscillator over $(r - r_0)$; l, m are quantum numbers for the spherical harmonics, Y_{lm}; A is any operator contributing to the hamiltonian (16). These matrix elements are discussed in appendix C. Comparing the hamiltonian (16) and expressions (C.6)–(C.11) leads to the inclusion into H_r of some additional terms arising from formula (C.6). In such a case H_r has the form

$$H_r = -\frac{1}{2\mu_2}\frac{r_0^2}{b^2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{2\mu_2}\frac{r_0^2(b^2 - a^2)}{a^2b^2}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\cos\theta + V_r(r) . \tag{17}$$

This expression of the operator is not good for the simple variational method due to the parametrical dependence on the angle θ. Nevertheless it may be used if the adiabatic approximation for the separation of radial and angular variables is applicable. This approximation will be considered separately and here we limit ourselves to the simple factorization method and use the auxiliary radial operator, H_r, of the form (7).

To obtain the bending rotation operator H_θ we average the hamiltonian (16) with the vibrational function describing the motion over the variable $(r - r_0)$. The resulting operator H_θ depends on the vibrational function used but we neglect such a dependence in the zero order approximation. Thus using (C.6)–(C.11) we obtain the following expression for the "rigid" bender-rotation operator:

$$\begin{aligned} H_\theta = &\frac{1}{2\mu_2 b^2}\left[L^2 + \frac{b^2-a^2}{a^2}(\sin^2\theta\, L^2 + L^2\sin^2\theta - 2L_z^2)\right] \\ &+ \frac{1}{2\mu_1 R_0^2}\left[J^2 + \frac{a^2}{b^2}L^2 + \frac{b^2-a^2}{b^2}(\sin^2\theta L^2 + L^2\sin^2\theta) + \frac{a^2-3b^2}{b^2}L_z^2\right. \\ &+ \tfrac{1}{2}\left(\frac{a^2-b^2}{ab}\right)^2(\sin^4\theta L^2 + L^2\sin^4\theta - 2\sin^2\theta L_z^2) - \frac{a}{b}(L_+J_- + L_-J_+) \\ &\left. - \frac{a^2-b^2}{ab}(\bar{E}_+J_- + \bar{E}_-J_+)\right] + V_\theta(\theta) + V_k(\theta)\,. \end{aligned} \tag{18}$$

Here $V_k(\theta)$ is the additional potential obtained from the averaging of the kinetic energy, $\bar{E}_\pm$ are the $E_\pm$ operators integrated over the radial variable. The kinematic potential has the form

$$\begin{aligned} V_k = &\frac{a^2-b^2}{4\mu_2 a^2 b^2}(1-3\cos^2\theta) + \frac{1}{4\mu_1 R_0^2}\left[\frac{a^2-b^2}{b^2}(1-3\cos^2\theta)\right. \\ &\left. + \left(\frac{a^2-b^2}{ab}\right)^2(\sin^4\theta - 12\sin^2\theta\cos^2\theta + 3\sin^2\theta)\right]. \end{aligned} \tag{19}$$

In conclusion to this section we briefly discuss the general method of finding eigenvalues and eigenfunctions of the operator (16).

(a) We diagonalize the operator H_r (using harmonic oscillator functions, for example).

(b) We diagonalize the operator H_θ in the basis

$$2^{-1/2}[D^J_{k0}Y_{lk}(\theta,\phi) \pm D^J_{-k0}Y_{l-k}(\theta,\phi)], \quad D^J_{00}Y_{l0}(\theta,\phi)\,,$$

where $D^J_{k0}(\alpha,\beta,0)$ are generalized spherical functions, depending on two Euler angles connecting the laboratory fixed frame and the body fixed one.

(c) The operator (16) is diagonalized in the basis obtained by multiplication of the eigenfunctions of the operators H_r and H_θ.

The method of solution is just the same as was used by us earlier [4]. The only disagreement is the most complicated form of operators adapted to some special cases of the potential energy surface.

2.2. Strong ellipticity

We can generalize the spherical model to the case of a strongly elliptical potential surface. Let a nonrigid trajectory be defined by

$$r_\theta = r(\theta) = r_0(1 + A_1\cos\theta + A_2\cos^2\theta + \ldots)$$

and the potential has the form

$$V(r,\theta) = \sum_{km} C_{km}(r - r_\theta)^k\cos^m\theta\,.$$

Here we use r_θ which depends on θ, in contrast to the potential (9) with constant r_0. In such a case we are to use some new auxiliary operators because the eigenfunctions of the operators (6) and (7) are not suitable for the basis construction. Instead of (6) we take

$$H_\theta = \frac{1}{2\mu_1 R_0}[L^2 + J^2 - (2L_z^2 + L_+J_- + L_-J_+)] + \tfrac{1}{2}\left(\frac{1}{2\mu_2 r_\theta^2}L^2 + L^2\frac{1}{2\mu_2 r_\theta^2}\right) + V_\theta(\theta)\,, \tag{20}$$

where

$$V_\theta(\theta) = \sum_m C_{0m} \cos^m \theta \,,$$

and we use the function B_θ depending on the angle θ instead of the rotational constant $(2\mu_2 r_0^2)^{-1}$

$$B_\theta = (2\mu_2 r_\theta^2)^{-1} \,.$$

We have to use the symmetrized product $(B_\theta L^2 + L^2 B_\theta)/2$ instead of $B_\theta L^2$ due to the hermitian property of the operator H_θ; the expression for H_r may be generalized in a similar manner

$$H_r = -\tfrac{1}{2}\mu_2^{-1}\, \partial^2/\partial r^2 + V(r - r_\theta) \,; \tag{21}$$

where

$$V_r(r - r_\theta) = \sum_k C_{k0}(r - r_\theta)^k \,.$$

The eigenvalue of (21) does not depend on θ if we increase the integration range from $(0, \infty)$ to $(-\infty, \infty)$, but the eigenfunction is a function of θ even in this case. The total problem may be resolved by using basis functions which are products of the eigenfunctions for operators (20) and (21).

2.3. Hamiltonian in elliptical coordinates

Sometimes the potential energy may be expressed in a rather simple form in the elliptical coordinates λ, μ:

$$V(\lambda, \mu) = \sum_{k,m} (\lambda - \lambda_0)^k \mu^m \,, \tag{22}$$

such that

$$V(\lambda, \mu) = V_\lambda(\lambda) + V_\mu(\mu) + W(\lambda, \mu) \,,$$

and $W(\lambda, \mu)$ is a small term. In such a case it is desirable to use elliptical coordinates. The variables cannot be separated in elliptical coordinates with the potential of the form (22), but the simple potential is attractive for using such variables.

We transform now the total operator (5) into elliptical coordinates;

$$x = \tfrac{1}{2}R \cos \Phi \,[(\lambda^2 - 1)(1 - \mu^2)]^{1/2}, \quad y = \tfrac{1}{2}R \sin \phi \,[(\lambda^2 - 1)(1 - \mu^2)]^{1/2}, \quad z = \tfrac{1}{2}\lambda\mu R \,.$$

We use the change of variables which removes the weight factor. Thus

$$\iiint \Psi^*(\lambda, \mu, \phi)\Psi(\lambda, \mu, \phi)\, \mathrm{d}\lambda\, \mathrm{d}\mu\, \mathrm{d}\phi = 1 \,,$$

and the laplacian has the form

$$\Delta = \frac{R}{2}\left[\frac{8}{R^3(\lambda^2 - \mu^2)}\right]^{1/2} \left[\frac{\partial}{\partial\lambda}(\lambda^2 - 1)\frac{\partial}{\partial\lambda} + \frac{\partial}{\partial\mu}(1 - \mu^2)\frac{\partial}{\partial\mu} + \frac{\partial}{\partial\phi}\frac{(\lambda^2 - \mu^2)}{(\lambda^2 - 1)(1 - \mu^2)}\frac{\partial}{\partial\phi}\right]\left[\frac{8}{R^3(\lambda^2 - \mu^2)}\right]^{1/2} . \tag{23}$$

To transform the operators $L_\pm$ and L_z we introduce in accordance with ref. [13] the following abbreviations

$$\hat{a} = [(\lambda^2 - 1)(1 - \mu^2)/(\lambda^2 - \mu^2)]^{1/2}(\mu\partial/\partial\lambda - \lambda\partial/\partial\mu)(\lambda^2 - \mu^2)^{-1/2}, \quad \hat{b} = \lambda\mu/[(\lambda^2 - 1)(1 - \mu^2)]^{-1/2} . \tag{24}$$

Then

$$L_z = -\mathrm{i}\partial/\partial\phi, \quad L_\pm = \exp(\pm\mathrm{i}\phi)(\pm\hat{a} + \mathrm{i}\hat{b}\,\partial/\partial\phi), \quad L^2 = L_z^2 + \tfrac{1}{2}(L_+L_- + L_-L_+)\,. \tag{25}$$

So eqs. (23)(25) give the total operator representation in elliptical variables.

We divide now the total hamiltonian to form the auxiliary operators H_λ and H_μ. Such a separation is obvious for the potential energy but not trivial for the kinetic energy. The standard method for obtaining the H_μ operator is to put λ equal λ_0 in the total hamiltonian and extract all terms which do not contain derivatives with respect to λ.

To do this we introduce

$$\hat{a}^0 = [(\lambda_0^2 - 1)(1-\mu^2)/(\lambda_0^2 - \mu^2)]^{1/2}(-\lambda_\rho\partial/\partial\mu)(\lambda_0^2 - \mu^2)^{-1/2}\,,$$

$$\hat{b}^0 = \lambda_0\mu[(\lambda_0^2 - 1)(1-\mu^2)]^{-1/2}\,,.$$

$$L_\pm^0 = \exp(\pm\mathrm{i}\phi)(\pm\hat{a}^0 + \mathrm{i}b^0\partial/\partial\phi)\,,$$

$$A_\pm = \{[(\lambda_0^2 - 1)(1-\mu^2)]^{1/2}/(\lambda_0^2 - \mu^2)\}\mu\,\partial/\partial\lambda\,\exp(\pm\mathrm{i}\phi)\,.$$

Then we can write H_μ as

$$\begin{aligned} H_\mu = {} & \frac{1}{2\mu_1 R_0^2}\,[J^2 + L_z^2 + \tfrac{1}{2}(L_+^0L_-^0 + L_-^0L_+^0) - (2L_z^2 + L_+^0J_- + L_-^0J_+)] \\ & - \frac{1}{2\mu_2}\left[\frac{8}{R_0^3(\lambda_0^2 - \mu^2)}\right]^{1/2}\frac{R_0}{2}\left[\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial}{\partial\mu} + \frac{\partial}{\partial\phi}\frac{\lambda_0^2 - \mu^2}{(\lambda_0^2 - 1)(1-\mu^2)}\frac{\partial}{\partial\phi}\right] \\ & \times [8/R_0^3(\lambda_0^2 - \mu^2)]^{1/2} + V_\mu(\mu)\,. \end{aligned}$$

If we want now to construct H_λ it can easily be seen that the terms containing $\partial/\partial\lambda$ include a factor depending on μ. We cannot put $\mu = \mu_0$ because our model corresponds to an almost free motion over μ at fixed λ. Such a situation arises due to the complicated form of the kinetic energy operator in elliptical coordinates. It is preferable to use the H_λ operator which depends parametrically on μ, i.e. to use the adiabatic type factorization (see, for example ref. [17]). Thus

$$H_\lambda = \frac{1}{2\mu_1 R_0^2}\left[\frac{(\lambda^2 - 1)(1-\mu^2)}{(\lambda^2 - \mu^2)^2}\mu^2\frac{\partial^2}{\partial\lambda^2}\right] - \frac{1}{2\mu_2}\frac{4(\lambda^2 - 1)}{R_0^2(\lambda^2 - \mu^2)}\frac{\partial^2}{\partial\lambda^2} + V_\lambda(\lambda)\,,$$

and we must solve a μ-equation of the type

$$[H_\mu + E_N(\mu)]\chi(\mu) = E\chi(\mu)\,,$$

where $E_N(\mu)$ is the eigenvalue of the H_λ operator. The last method may easily be used only in the case when zero-order functions (i.e. products of the eigenfunctions of H_λ and H_μ) are a good approximation to the total problem. To simplify the hamiltonian H_λ we can put all λ in the kinetic energy expression equal to λ_0.

3. Conclusion

We have constructed and simplified hamiltonians for triatomic nonrigid molecules with a diatomic rigid core. This extensive study was performed because we hope to treat the general problem of the vibration–rotation spectra for nonrigid inorganic molecules in the gas phase. Unfortunately the experimental investigations of ionic inorganic molecules in the gas phase are not numerous [18]. We hope that the purely theoretical models presented here will facilitate the understanding of the general qualitative structure of the vibration–rotation spectra of ionic nonrigid molecules and will give possibilities for the interpretation of future data and for the theoretical prediction of thermodynamic properties of similar molecules at high temperatures. The triatomics are the most simple molecules for manipulating with the total hamiltonian and searching the most simple models. The equations obtained may be rather easily generalized to more complex molecules. We have not repeated here the numerical calculations because some of them for the LiCN type molecule have already been published [4]. The following important step is to take into account the possible symmetry of the rigid core. This is important for a large number of inorganic nonrigid salts with symmetrical rigid core. ($LiBH_4$ is an appropriate example.)

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Appendix A

We develop here the hamiltonian in the body fixed coordinate frame, connected with the vector $\bar{r}$. Such a choice of the moving frame is more suited in the case of van der Waals molecules because the vibration–rotation interaction may be taken into account by perturbation theory in this case. The hamiltonian (3) has now the form

$$H = -\frac{1}{2\mu_1}\Delta_{\bar{R}} - \frac{1}{\mu_2}\left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\left[J^2 + L_{\bar{R}}^2 - (2L_z^2 + L_+J_- + L_-J_+)\right]\right\} + V(R, r, \theta) ,$$

where J is the total angular momentum, $L_{\bar{R}}$ is the angular momentum associated with the vector $\bar{R}$. Averaging this operator over R we obtain the following analog of the hamiltonian (5)

$$H = -\frac{1}{2\mu_2}\frac{d^2}{dr^2} + \frac{L_{\bar{R}}^2}{2\mu_1 R_0^2} + \frac{1}{2\mu_2 r^2}\left[J^2 + L_{\bar{R}}^2 - (2L_z^2 + L_+J_- + L_-J_+)\right] + V(r, \theta) . \tag{A.1}$$

To elaborate the model adapted to the elliptical potential it is desirable to transform the operator in the same way as in (8). But we cannot apply the same change of variables due to the use of spherical variables.

Let the nonrigid trajectory be described by the relation

$$r(\theta) = r_0(1 + A_1 \cos\theta + A_2 \cos^2\theta + ...) ,$$

where $A_1, A_2, ...$ are constants. Then the transformation

$$r' = r[1 + A_1 \cos\theta + A_2 \cos^2\theta + ...]^{-1}, \quad \theta' = \theta ;$$

(r', θ' are the new variables) results in a new nonrigid trajectory which is a circle. The transformation of the hamiltonian (A.1) to new variables is straightforward but does not yield such compact form for the hamiltonian as expression (16).

Appendix B

For the case of non-coincidence of the center of the elliptical potential surface and the center of mass of the rigid core we use the generalized internal hamiltonian (see eq. (5) of ref. [4])

$$H_\kappa = -\left(\frac{\kappa^2}{8\mu_1} + \frac{1}{2\mu_2}\right)\Delta_{\bar{r}} + \frac{1}{2\mu_1 R_0^2}(J^2 + L^2) - \frac{1}{2\mu_1 R_0^2}(2L_z^2 + L_+J_- + L_-J_+)$$
$$-(\kappa/8\mu_1 R_0)\,[P_+L_- + P_-L_+ + L_-P_+ + L_+P_- - 2(P_+J_- + P_-J_+)] + V(r,\theta)\,, \tag{B.1}$$

where

$$P_\pm = \pm \mathrm{i}P_x - P_y = \pm\partial/\partial x + \mathrm{i}\,\partial/\partial y, \quad \kappa = (m_\mathrm{b} - m_\mathrm{a})/(m_\mathrm{a} + m_\mathrm{b}) - (\beta_\mathrm{b} - \beta_\mathrm{a})/(\beta_\mathrm{a} + \beta_\mathrm{b});$$

$\beta_\mathrm{a}, \beta_\mathrm{b}$ are some parameters. The $\bar{r}$ vector is defined now by the relation

$$\bar{r} = \bar{r}_\mathrm{c} - (\beta_\mathrm{a}\bar{r}_\mathrm{a} + \beta_\mathrm{b}\bar{r}_\mathrm{b})/(\beta_\mathrm{a} + \beta_\mathrm{b})\,.$$

The case $\kappa = 0$ corresponds to the hamiltonian (4). To transform the hamiltonian (B.1) into new variables (8) we make use of formulae (10), (14), (15) and the relation

$$P_\pm \to (r_0/b)P_\pm\,.$$

Denoting by H_E the hamiltonian (16) we obtain the following generalized operator for the case $\kappa \neq 0$

$$H = H_E - \frac{\kappa^2}{8\mu_1}\left[\frac{r_0}{b^2}\Delta_{\bar{r}} + \frac{r_0^2(b^2 - a^2)}{a^2b^2}\frac{\partial^2}{\partial z^2}\right] - \frac{\kappa}{8\mu_1 R_0}\left[\frac{ar_0}{b^2}(P_+L_- + P_-L_+ + L_-P_+ + L_+P_-)\right.$$
$$\left. + \frac{(a^2 - b^2)r_0}{ab^2}(P_+E_- + P_-E_+ + E_-P_+ + E_+P_-) - \frac{2r_0}{b}(P_+J_- + P_-J_+)\right].$$

Appendix C

Some matrix elements of the type $\langle n'l'm'|A|nlm\rangle$ are listed below. Here n is the quantum number for the oscillator over the variable $(r - r_0)$, l is the quantum number associated with the spherical harmonics Y_{lm}, A is some operator contributing to the hamiltonian (16).

First of all we transform the operators $E_\pm$ and $\partial/\partial z$

$$E_\pm = \pm r\sin\theta\exp(\pm \mathrm{i}\phi)\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right), \tag{C.1}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}, \tag{C.2}$$

to remove the weight factor r^2. It is needed to make the transformation

$$\partial/\partial r \to (\partial/\partial r - 1/r)\,.$$

Then we have $\sin\theta$ as the weight factor and the expressions (C.1) and (C.2) take the form

$$E_\pm = \pm r\sin\theta\exp(\pm \mathrm{i}\phi)\left[\cos\theta\left(\frac{\partial}{\partial r} - \frac{1}{r}\right) - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right]; \tag{C.3}$$

$$\partial/\partial z = \cos\theta\,\partial/\partial r - r^{-1}(\cos\theta + \sin\theta\,\partial/\partial\theta)\,. \tag{C.4}$$

Now we can calculate the matrix elements:

$$\langle n'l'm'|\partial^2/\partial z^2|nlm\rangle$$
$$= \langle n'|\mathrm{d}^2/\mathrm{d}r^2|n\rangle\langle l'm'|\cos^2\theta|lm\rangle - \langle n'|r^{-2}|n\rangle\langle\sin\theta(\partial/\partial\theta)l'm'|\sin\theta(\partial/\partial\theta)lm\rangle \tag{C.5}$$
$$+ \langle(\partial/\partial r - r^{-1})n'|r^{-1}n\rangle\langle\cos\theta\, l'm'|\sin\theta(\partial/\partial\theta)lm\rangle + \langle r^{-1}n'|(\partial/\partial r - r^{-1})n\rangle\langle\sin\theta(\partial/\partial\theta)l'm'|\cos\theta\, lm\rangle\,.$$

This expression is suitable for the calculation due to simple recurrence relations for $\cos\theta\, Y_{lm}$ and $\sin\theta(\partial/\partial\theta)\, Y_{lm}$ [16]. For diagonal matrix elements we have

$$\langle nl'm'|\partial^2/\partial z^2|nlm\rangle = \langle n|\mathrm{d}^2/\mathrm{d}r^2|n\rangle\langle l'm'|\cos^2\theta|lm\rangle + \langle n|r^{-2}|n\rangle\langle l'm'|$$

$$-\tfrac{1}{2}(\sin^2\theta L^2 + L^2\sin^2\theta) + L_z^2 + \tfrac{1}{2}(1-3\cos^2\theta)|lm\rangle\,. \tag{C.6}$$

Some other matrix elements may be calculated as well:

$$\langle nl'm'|L_+E_- + L_-E_+ + E_+L_- + E_-L_+|nlm\rangle$$

$$= \langle l'm'|(1-3\cos^2\theta) - 2(\sin^2\theta L^2 + L^2\sin^2\theta) + 4L_z^2|lm\rangle \;\ldots\,, \tag{C.7}$$

$$\langle nl'm'|E_+E_- + E_-E_+|nlm\rangle = \langle l'm'|\sin^4\theta L^2 + L^2\sin^2\theta L_z^2 - 12\sin^2\theta\cos^2\theta$$

$$+ \sin^4\theta + 3\sin^2\theta|lm\rangle + 2\langle r(\partial/\partial r)n|r(\partial/\partial r)n\rangle\langle l'm'|\sin^2\theta\cos^2\theta|lm\rangle\,. \tag{C.8}$$

To evaluate matrix elements of the operator $E_+J_- + E_-J_+$ we define the operators $\bar{E}_\pm$

$$\bar{E}_\pm = \langle n|E_\pm|n\rangle\,. \tag{C.9}$$

Taking into consideration eq. (3.3) and the properties of harmonic oscillator functions we obtain

$$\bar{E}_\pm = \mp\sin\theta\, \mathrm{e}^{\pm\mathrm{i}\phi}(\tfrac{3}{2}\cos\theta + \sin\theta\,\partial/\partial\theta), \quad (\bar{E}_\pm)^+ = \bar{E}_\mp\,, \tag{C.10}$$

$$\langle nl'm'|E_+J_- + E_-J_+|nlm\rangle = \langle l'm'|\bar{E}_+J_- + \bar{E}_-J_+|lm\rangle\,. \tag{C.11}$$

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