Simulation of high-excited RV states of triatomic XY_2 (C_{2v}) molecules

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The model problems for high-exited ro-vibrational states of triatomic molecules such as H_2O, CH_2, NH_2, and hydrogen ion H_3^+ are considered. The model approach is based on an iterative solution of the Schrödinger equation by successive improvement of "trial" wave functions. These trial wave functions are eigenfunctions of some reduced, exactly solvable Hamiltonian, describing a particular motion in the molecule: bending or stretching vibration and molecular rotation.

Introduction

The need in simple models for describing the rotational-vibrational (RV) energy spectra of triatomic molecules, such as H_2O, H_2S, or H_3^+, is caused by that the available methods of calculation of the effective Hamiltonians (variational method[1] and the perturbation method[2]) face significant difficulties if applied to high-excited states. The direct variational method has no principal limitations, which could hamper its application to high-excited states, and this is its advantage over other methods. However, it provides for the numerical results, which create certain difficulties in the analysis. For example, the energy levels and wave functions for high RV states of H_2O near the dissociation threshold were calculated in Ref. 3, but the results were analyzed only visually, which, certainly, is indicative of the considerable difficulty of interpretation of such numerical data.

The methods of effective Hamiltonians, in its turn, though having significant advantages of the simplicity of calculations and interpretation of the results, are restricted to small perturbations, and their use for high-excited states requires certain modification, in particular, the improvement of the initial approximation or the use of special methods for summation of divergent series.

As known, for triatomic molecules of a certain type, for example, for molecules like H_2O and H_2S, the simple, exactly solvable models, for example, Morse or Poschl–Teller oscillator, well describe qualitatively (and quantitatively in some cases) the transformation of vibrational or ro-vibrational energy spectra upon the transition from low to high-excited states. Such models are used, for example, to justify the local mode approach[4] and the four-level clusterization[5] or to explain the phenomenon of monodromy.[6] At the same time, simplification of these models is strongly desirable for them to account for the vibrational-rotational interaction in high-excited states sufficiently accurate.

The self-consistent procedure of solving the Schrödinger equation, proposed earlier by Makarewicz[7] used the exactly solvable one-dimensional models, which allowed the qualitative analysis of bending-rotational states of the H_2O molecule. In this paper, the idea of self-consistent calculations and the exactly solvable problems: Kratzer and Poschl–Teller oscillators, are applied to construct simple models, describing the energy spectrum of triatomic molecules. In contrast to Refs. 7 and 8, we consider the complete problem, that is, take into account all the three types of vibrations (stretching symmetric and antisymmetric, bending) and rotation of the molecule. It is worthy to note Ref. 9, which proposes new exactly solvable models for describing the vibrational states of the triatomic molecules.

1. Molecular Hamiltonian in natural coordinates

The Hamiltonian of a triatomic molecule in natural coordinates has the form[1]:

$$H = T_S + T_{RB} + T_C + T_M + U(\rho_1, \rho_2, z). \qquad (1)$$

The operator T_S represents the kinetic energy associated with stretching vibrations:

$$T_S = b_1 p_1^2 + b_2 p_2^2 + 2b_0 z p_1 p_2. \qquad (2)$$

The bending-rotational part of the kinetic energy can be expressed as

$$T_{RB} = b_+(\rho_1\rho_2)[p_z(1-z^2)p_z + a(z)J_z^2 + b(z)J_x^2 + cJ_y^2]. \qquad (3)$$

The operator

$$T_C = \frac{1}{2}b_-(\rho_1\rho_2)\{(1-z^2)^{1/2}, p_z\}J_y - \\ -\frac{1}{2}b_-(\rho_1\rho_2)(1-z^2)^{-1/2}\{J_x, J_z\} \qquad (4)$$

is due to the Coriolis interaction, and

$$T_{\mathrm{M}} = b_{12}(\rho_1\rho_2)[\frac{1}{2}\{z, \hat{p}_z(z^2-1)p_z\} + a(z)J_z^2 - b(z)J_x^2 + czJ_y^2] +$$
$$+ G\{1-z^2, p_z\} - (1-z^2)^{1/2}GJ_y. \qquad (5)$$

Here

$$b_{\pm}(\rho_1\rho_2) = \frac{b_1}{\rho_1^2} \pm \frac{b_2}{\rho_2^2}, \qquad (6)$$

$$b_{12}(\rho_1\rho_2) = \frac{2b_0}{\rho_1\rho_2}; \qquad (7)$$

$$G = b_0(\rho_2^{-1}p_1 + \rho_1^{-1}p_2); \qquad (8)$$

$$a(z) = \frac{1}{2(1+z)}; \quad b(z) = \frac{1}{2(1-z)}; \quad c = \frac{1}{4}; \qquad (9)$$

$$b_i = \frac{h}{8\pi^2 c\mu_i r_{\mathrm{e}}^2}; \quad \frac{1}{\mu_i} = \frac{1}{m_i} + \frac{1}{M}; \quad b_0 = \frac{h}{8\pi^2 cMr_{\mathrm{e}}^2}; \qquad (10)$$

$$p_i = -i\partial/\partial\rho_i, \; p_z = -i\partial/\partial z, \; \rho_i = r_i/r_{\mathrm{e}},$$
$$z = \cos\theta \; (0 \le \rho_i \le \infty, \; -1 \le z \le 1)$$

are the dimensionless vibrational coordinates; r_i is the length of the ith bond (i = 1, 2), r_{e} is its equilibrium value; θ is the angle between the bonds; $\{A, B\} = AB + BA$ denotes the anticommutator; $U(\rho_1, \rho_2, z)$ is the potential energy function. The molecule-fixed coordinate system is chosen so that its origin lies at the center of gravity, the axis y is perpendicular to the plane of the molecule (plane xz), and the axis x is directed along the bisector of the angle θ.

2. Determination of the RV wave functions and energy levels by the method of self-consistent calculations

Assume that the rotational-vibrational wave functions can be presented by a product of three functions

$$\Psi_{Ivr}(\rho, z, \Omega) = \phi_I^{[vr]}(\rho)\varphi_v^{[Ir]}(z)\chi_r^{[Iv]}(\Omega), \qquad (11)$$

each depending on one type of coordinates: rotational $\Omega = \{\alpha, \beta, \gamma\}$ and vibrational stretching $\rho = \{\rho_1, \rho_2\}$ or bending z. The quantum numbers in Eq. (11) are determined from a particular procedure of calculations, which consists in the following.

The wave functions $\Psi_{Ivr}(\rho, z, \Omega)$ should satisfy the Schrödinger equation:

$$H\phi_I^{[vr]}(\rho)\varphi_v^{[Ir]}(z)\chi_r^{[Iv]}(\Omega) =$$
$$= E_{Ivr}\phi_I^{[vr]}(\rho)\varphi_v^{[Ir]}(z)\chi_r^{[Iv]}(\Omega). \qquad (12)$$

Equation (12) allows us to obtain three equations for determination of $\phi_I^{[vr]}(\rho)$, $\varphi_v^{[Ir]}(z)$, and $\chi_r^{[Iv]}(\Omega)$. Multiplying Eq. (12) by any two functions of the product (11) and integrating over the corresponding variables, we obtain three equations:

$$\tilde{H}_{\mathrm{S}}^{[vr]}\phi_I^{[vr]}(\rho) = E_I^{[vr]}\phi_I^{[vr]}(\rho),$$
$$\tilde{H}_{\mathrm{B}}^{[Ir]}\varphi_v^{[vr]}(z) = E_v^{[Ir]}\varphi_v^{[Ir]}(z), \qquad (13)$$
$$\tilde{H}_{\mathrm{R}}^{[Iv]}\chi_r^{[Iv]}(\Omega) = E_r^{[Iv]}\chi_r^{[Iv]}(\Omega),$$

where the “effective” operators $\tilde{H}_{\mathrm{S}}^{[vr]}$, $\tilde{H}_{\mathrm{B}}^{[Ir]}$, $\tilde{H}_{\mathrm{R}}^{[Iv]}$ are determined as the mean values of the complete Hamiltonian:

$$\tilde{H}_{\mathrm{S}}^{[vr]} = \left\langle \varphi_v^{[Ir]}\chi_r^{[Iv]} \middle| H \middle| \varphi_v^{[Ir]}\chi_r^{[Iv]} \right\rangle,$$
$$\tilde{H}_{\mathrm{B}}^{[Ir]} = \left\langle \phi_I^{[vr]}\chi_r^{[Iv]} \middle| H \middle| \phi_I^{[vr]}\chi_r^{[Iv]} \right\rangle, \qquad (14)$$
$$\tilde{H}_{\mathrm{R}}^{[Iv]} = \left\langle \phi_I^{[vr]}\varphi_v^{[Ir]} \middle| H \middle| \phi_I^{[vr]}\varphi_v^{[Ir]} \right\rangle.$$

The system of equations (13) will be solved by iterations. At the first stage, to determine the effective operators, the functions of some zeroth approximation are used, matrix elements are calculated in Eq. (14), and Eq. (13) is used to determine the new approximation $\phi_I^{[vr]}(\rho)$, $\varphi_v^{[Ir]}(z)$, $\chi_r^{[Iv]}(\Omega)$, by use of which it is possible to find new effective operators, and so on. The procedure is repeated until the energy differences

$$E_I^{[vr]} - E_v^{[Ir]}, \; E_I^{[vr]} - E_r^{[Iv]}, \; E_v^{[Ir]} - E_r^{[Iv]}, \qquad (15)$$

obtained from solution of three equations (13) for eigenvalues become small enough.

The convergence of the iteration procedure depends on many factors, in particular, on the possibility of representing the wave function of a given RV state in the form of a product of three functions. Note that, as was shown in Ref. 7, the self-consistent procedure converges for high-excited bending-rotational states of molecules like water.

The operators determined by Eqs. (14) depend on all quantum numbers of the initial-approximation functions. For example, the Hamiltonian $\tilde{H}_{\mathrm{S}}^{[vr]}$ depends, naturally, on the quantum numbers v and r ($r \equiv JK_aK_c$), but also on the quantum number I ($I \equiv nm\sigma$, $\sigma = \pm 1$ are the quantum numbers of the local-mode model). Thus, in the process of calculations, upon selection of a certain RV state of the molecule (that is, the set of quantum numbers Ivr) it is needed to determine the necessary matrix elements and to solve the problem for eigenvalues of the operator $\tilde{H}_{\mathrm{S}}^{[vr]}$..

The method of calculation of RV energy levels proposed here is the generalization of the method of self-consistent calculations of bending-rotational states of triatomic molecules[7,8] for the complete RV problem. It should be emphasized that this method is not exact; moreover, the wave functions (11) are mutually orthogonal only for the states corresponding to different values of the angular momentum quantum number or to different symmetries. For states of the same symmetry, they are not orthogonal, but can be orthogonalized whenever necessary with the use of the standard Gramm–Schmidt procedure.

It is essential that the method allows one to construct simple models for description of RV wave functions and energy levels.

Assume now that two of the wave functions (11), for example $\phi_I^{[vr]}(\rho)$ and $\varphi_v^{[Ir]}(z)$, are known. In this case, the third function $\chi_r^{[Iv]}(\Omega)$ (and the energy level) is determined from the third equation (14). If the wave functions $\phi_I^{[vr]}(\rho)$, $\varphi_v^{[Ir]}(z)$ are calculated as approximate solutions of the first two equations (14), for example, in the form of the model problems accounting for molecular rotation, then they depend on the set of some parameters caused by RV interaction in the molecule. Consequently, the effective Hamiltonian $\tilde{H}_{\mathrm{R}}^{[Ir]}$ must depend on the same parameters. It is obvious that this approach, directly following from the self-consistent procedure, permits the construction of rather complex models for calculation of rotational energy levels. If the initial model functions $\phi_I^{[vr]}(\rho)$ and $\varphi_v^{[Ir]}(z)$ are chosen more or less realistic, then this approach can give rather accurate calculated energy levels.

3. Models for describing RV states of triatomic molecules

Consider the effective operators (14) in a more detail. As follows from Eqs. (1)–(10), they can be represented as

$$\tilde{H}_{\mathrm{S}}^{[vr]} = b_1 p_1^2 + b_2 p_2^2 + 2b_0 p_1 p_2 < z >_v + < U(\rho_1, \rho_2, z) >_v + \\ + < T_{\mathrm{RB}} >_{vr} + < T_{\mathrm{C}} >_{vr} + < T_{\mathrm{M}} >_{vr}, \tag{16}$$

$$\tilde{H}_{\mathrm{B}}^{[Ir]} = < b_+(\rho_1\rho_2) >_{Ir} \left[p_z(1-z^2)p_z + a(z) < J_z^2 >_r + \right. \\ \left. + b(z) < J_x^2 >_r + c < J_y^2 >_r \right] + < U(\rho_1, \rho_2, z) >_I + \\ + < T_{\mathrm{S}} >_{Ir} + < T_{\mathrm{C}} >_{Ir} + < T_{\mathrm{M}} >_{Ir}, \tag{17}$$

$$\tilde{H}_{\mathrm{R}}^{[Iv]} = < b_+(\rho_1\rho_2) >_I [< p_z(1-z^2)p_z >_v + < a(z) >_v J_z^2 + \\ + < b(z) >_v J_x^2 + cJ_y^2] + < T_{\mathrm{S}} >_{Iv} + < T_{\mathrm{C}} >_{Iv} + < T_{\mathrm{M}} >_{Iv} + \\ + < U(\rho_1, \rho_2, z) >_{Iv}. \tag{18}$$

In Eqs. (16)–(18), one can separate out some main part and additions due to the interactions between the motions of different types.

a) Consider first the operator $\tilde{H}_{\mathrm{S}}^{[vr]}$, describing the stretching vibrations. Obviously, it can be presented in the form

$$\tilde{H}_{\mathrm{S}}^{[vr]} = b_1 p_1^2 + b_2 p_2^2 + 2b_0 p_1 p_2 < z >_v + < U(\rho_1, \rho_2, z) >_v + \\ + b_+(\rho_1\rho_2) A_{\mathrm{S}}(v, r) + b_-(\rho_1\rho_2) B_{\mathrm{S}}(v, r) + \\ + b_{12}(\rho_1\rho_2) C_{\mathrm{S}}(v, r) + G D_{\mathrm{S}}(v, r), \tag{19}$$

where the operator G is described by Eq. (8) and

$$A_{\mathrm{S}}(v, r) = < p_z(1-z^2)p_z >_v + < a(z) >_v < J_z^2 >_r + \\ + < b(z) >_v < J_x^2 >_r + c < J_y^2 >_r; \tag{20}$$

$$B_{\mathrm{S}}(v, r) = \frac{1}{2} < \{(1-z^2)^{\frac{1}{2}}, \ p_z\} >_v < J_y >_r - \\ - \frac{1}{2} < (1-z^2)^{-\frac{1}{2}} >_v < \{J_x, J_y\} >_r; \tag{21}$$

$$C_{\mathrm{S}}(v, r) = \frac{1}{2} < \{z, p_z(z^2-1)p_z\} >_v + < a(z) >_v < J_z^2 >_r - \\ - < b(z) >_v < J_x^2 >_r + c < z >_v < J_y^2 >; \tag{22}$$

$$D_{\mathrm{S}}(v, r) = < \left\langle (1-z^2), \ p_z \right\rangle >_v - < (1-z^2)^{\frac{1}{2}} >_v < J_y >_r. \tag{23}$$

This Hamiltonian can be divided into two parts. The first part includes the first four terms of Eq. (19), determining the main part of the energy of stretching vibrations, while the rest operators determine some pseudopotential – the addition caused by the interaction of stretching vibrations with the bending vibration and the rotation of the molecule.

The first term in Eq. (20) is a v-dependent constant, while the following terms in this equation are functions of the rotational quantum numbers. The term $b_+(\rho_1\rho_2)A_{\mathrm{S}}(v, r)$ is, obviously, the v- and j-dependent centrifugal barrier to the dissociation in the potential energy curve of vibration of an individual bond (see also Ref. 8). This term is similar to the centrifugal barrier in the effective potential curve of diatomic molecules.

The next term $b_-(\rho_1\rho_2)B_{\mathrm{S}}(v, r)$ in Eq. (19) describes the Coriolis interaction between the stretching vibrations and rotation about the axis y of the molecular coordinate system. It can be seen that this term of the effective Hamiltonian, being antisymmetric with respect to the permutation of identical atoms, contributes only as the second-order value, and in the first-order approximation it can be neglected.[12]

The other terms of the effective Hamiltonian (19) are associated with the corrections caused by the displacements of the “central” atom in vibrations. In the case of $M \gg m_1$, m_2, they are small and can be neglected as well.

To estimate the order of $A_{\mathrm{S}}(v, r)$, let us use the simplest symmetric-top approximation. We obtain

$$A_{\mathrm{S}}(v, r) = < p_z(1-z^2)p_z >_v + < a(z) - \frac{b(z)+c}{2} >_v < J_z^2 >_r + \\ + < \frac{b(z)+c}{2} >_v < J^2 >_r + < \frac{b(z)-c}{2} >_v < J_{xy}^2 >_r, \tag{24}$$

where $J_{xy}^2 = J_x^2 - J_y^2$ and

$$< J_z^2 >_r = k^2, \quad < J^2 >_r = j(j+1);$$

$$b_0 < a(z) >_v \approx A_{0v0}, \quad b_0 < b(z) >_v \approx B_{0v0}. \tag{25}$$

Thus, the "main" part of the centrifugal addition to the stretching part of the potential has the form

$$\frac{1}{\rho_i^2}\left(A_{0v0}k^2+B_{0v0}j(j+1)\right). \qquad (26)$$

Since for light molecules like water the rotational constant, corresponding to the smallest moment of inertia, increases quickly with the increase of the quantum number v, achieving the values on the order of 10^3 cm^{-1} (Ref. 10), this term should be taken into account already in the first approximation.

For determination of the eigenvalues and eigenfunctions of the stretching Hamiltonian (19), it is convenient to use the model Kratzer potential for an individual bond

$$U_{\text{K}}(\rho)=E_{\text{d}}(1-\rho^{-1})^2, \qquad (27)$$

where E_{d} is the dissociation energy; the centrifugal part of the pseudopotential is taken into account as well. The energy levels in the zeroth approximation are determined by the equation

$$E_n^{\text{K}}=\frac{E_{\text{d}}}{b_{\text{e}}}\left[1-\frac{d^2}{\{n+1/2+\sqrt{d^2+A_{\text{S}}(v,r)+1/4}\}^2}\right]. \qquad (28)$$

The total energy is the sum $E_n^{\text{K}}+E_m^{\text{K}}$. The wave function has the form

$$S_n(\tilde{r})=N_n\tilde{r}^j e^{-\frac{\tilde{r}}{2}}L_n^{(2j+1)}(\tilde{r}), \qquad (29)$$

where

$$\tilde{r}=\rho\frac{2d}{n+A_{\text{S}}(v,r)+1}; \qquad (30)$$

$$d^2=E_{\text{d}}/b_{\text{e}}; \qquad (31)$$

$$j=\sqrt{d^2+A_{\text{S}}(v,r)+1/4}-1/2 \qquad (32)$$

and $L_n^{(\alpha)}(x)$ are the associated Legendre polynomials. The wave function is determined as a symmetrized product of the functions (29).

Thus, Eq. (28) describes a simple model for the RV energy spectrum of a triatomic molecule. It is significant that the energy depends on the rotational quantum numbers and the quantum number of the bending vibration. It is possible to represent A_{S}, determining the model, as the series expansions

$$A_{\text{S}}(v,r)=e_v+a_kK_a^2+a_JJ(J+1)+\ldots,$$

and to determine the parameters e_v, a_K, a_j, ... by fitting to the experimental energy levels. Equations (28)–(32) can easily be refined, by introducing other terms of the Hamiltonian $\tilde{H}_{\text{S}}^{[vr]}$, for example, $b_{-}(\rho_1\rho_2)B_{\text{S}}(v, r)$, into the consideration, as well as by using the two-level approximation to take into account the splitting of local pairs of states. The calculations made with the use of the model described will be reported in the papers that will follow.

From Eqs. (26) and (28) it follows that the energy of the stretching vibrations at quite a strong excitation can vary widely, because, as was already mentioned, $A_{\text{S}}(v, r)$ can strongly increase at the excitation of the bending vibration. The wave functions (29) also become strongly deformed at the excitation of the bending vibrations, which is stipulated by the dependence of $\tilde{r}$ and j on $A_{\text{S}}(v, r)$.

b) Consider now the effective Hamiltonian $\tilde{H}_{\text{B}}^{[Ir]}$, describing the bending vibrations. It follows from Eqs. (14) that

$$\begin{aligned}\tilde{H}_{\text{B}}^{[Ir]}=&<b_{+}(\rho_1\rho_2)>_I[p_z(1-z^2)p_z+\\&+a(z)<J_z^2>_r+b(z)<J_x^2>_r+c<J_y^2>_r]+\\&+<U(\rho_1,\rho_2,z)>_I+\{(1-z^2)^{\frac{1}{2}},p_z\}A_{\text{B}}(I,r)+\\&+(1-z^2)^{-\frac{1}{2}}B_{\text{B}}(I,r)+\frac{1}{2}\{z,p_z(z^2-1)p_z\}<b_{12}(\rho_1\rho_2)>_I+\\&+a(z)C_{\text{B}}(I,r)-b(z)D_{\text{B}}(I,r)+czE_{\text{B}}(I,r)+\\&+\{1-z^2,p_z\}F_{\text{B}}(I,r)+(1-z^2)^{\frac{1}{2}}L_{\text{B}}(I,r)+\\&+<p_1^2>_I+<p_2^2>_I+2b_0<z>_v<p_1p_2>_I,\end{aligned} \qquad (33)$$

where

$$A_{\text{B}}(I,r)=\frac{1}{2}<b_{-}(\rho_1\rho_2)>_I<J_y>_r; \qquad (34)$$

$$B_{\text{B}}(I,r)=-\frac{1}{2}<b_{-}(\rho_1\rho_2)>_I<\{J_x,J_z\}>_r; \qquad (35)$$

$$C_{\text{B}}(I,r)=<b_{12}(\rho_1\rho_2)>_I<J_z^2>; \qquad (36)$$

$$D_{\text{B}}(I,r)=<b_{12}(\rho_1\rho_2)>_I<J_x^2>_r; \qquad (37)$$

$$E_{\text{B}}(I,r)=<b_{12}(\rho_1\rho_2)>_I<J_y^2>_r; \qquad (38)$$

$$F_{\text{B}}(I)=b_0<(\rho_2^{-1}p_1+\rho_1^{-1}p_2)>_I; \qquad (39)$$

$$L_{\text{B}}(I,r)=-b_0<(\rho_2^{-1}p_1+\rho_1^{-1}p_2)>_I<J_y>_r. \qquad (40)$$

In the operator (33) we can separate out two parts:

$$\tilde{H}_{\text{B}}^{[Ir]}=FB(I)\tilde{H}_{\text{PT}}^{[Ir]}+\Delta\tilde{H}_{\text{B}}^{[Ir]}, \qquad (41)$$

where $FB(I)=<b_{+}(\rho_1\rho_2)>_I$. The first term $FB(I)\tilde{H}_{\text{PT}}^{[Ir]}$ is the main part of the energy, and the second one $\Delta\tilde{H}_{\text{B}}^{[Ir]}$ can be considered a small addition and neglected in the first approximation.

Then, let us perform some obvious transformations of the operator $\tilde{H}_{\text{PT}}^{[Ir]}$:

$$\begin{aligned}\tilde{H}_{\text{PT}}^{[Ir]}=&<b_{+}(\rho_1\rho_2)>_I\left[p_z(1-z^2)p_z+\left(a(z)-\frac{b(z)+c}{2}\right)<J_z^2>_r+\right.\\&\left.+\left(\frac{b(z)+c}{2}\right)<J^2>_r+\left(\frac{b(z)-c}{2}\right)<J_x^2-J_y^2>_r\right].\end{aligned} \qquad (42)$$

Introducing the model Poschl–Teller potential function

$$U_{\text{PT}}(z)=\frac{\beta_0^2}{2(1+z)}+\frac{\alpha_0^2}{2(1-z)} \qquad (43)$$

with the parameters α_0^2 and β_0^2, taken so that they ensure the best description of the vibrational energy of the bending oscillations, we obtain:

$$\tilde{H}_{\mathrm{PT}}^{[Ir]} = p_z(1-z^2)p_z + \frac{\beta^2(I,r)}{2(1+z)} + \frac{\alpha^2(I,r)}{2(1-z)} + c < J_y^2 >_r, \quad (44)$$

where

$$\alpha(I,r) = \left\{ \alpha_0^2 + \left[1 - \frac{< b_{12}(\rho_1\rho_2) >_I}{< b_+(\rho_1\rho_2) >_I} \right] < J_x^2 >_r \right\}^{1/2}; \quad (45)$$

$$\beta(I,r) = \left\{ \beta_0^2 + \left[1 + \frac{< b_{12}(\rho_1\rho_2) >_I}{< b_+(\rho_1\rho_2) >_I} \right] < J_z^2 >_r \right\}^{1/2}. \quad (46)$$

In accordance with the above-said, the model potential (41) is also subtracted in the operator $\Delta\tilde{H}_{\mathrm{B}}^{[Ir]}$. The Schrödinger equation with this effective operator has the exact solution in the form

$$E_v(I,r) = < b_+(\rho_1\rho_2) >_I \left\{ \left[v + \frac{\alpha(I,r)+\beta(I,r)}{2} \right] \times \right.$$

$$\left. \times \left[v + \frac{\alpha(I,r)+\beta(I,r)}{2} + 1 \right] + c < J_y^2 >_r \right\}. \quad (47)$$

The wave function of the effective operator is:

$$\varphi_v^{[\alpha(I,r),\beta(I,r)]} = N_V (1-z)^{\frac{\alpha(I,r)}{2}} (1+z)^{\frac{\beta(I,r)}{2}} P_v^{[\alpha(I,r),\beta(I,r)]}(z), \quad (48)$$

where $P_v^{[\alpha,\beta]}(z)$ are Jacoby polynomials.

Thus, in the zeroth approximation the energy of the bending states is determined by the simple equation (47), in which the parameters (45) and (46) depend only on the rotational quantum numbers and the quantum numbers of the stretching vibrations. This means that Eq. (47) accounts for the effect of rotation and stretching vibrations, and the energies are certainly shifted with respect to the energy levels in the simple model of bending vibration. The wave function (46) also depends on the quantum numbers I and r, and, consequently, it is "distorted" by the interactions with the "stretching" vibrations and rotation of the molecule. This model is more flexible and, obviously, more accurate that the equations derived by Makarewicz.[7]

c) The effective Hamiltonian determining the rotational part of the total wave function can be presented in the form

$$\tilde{H}_{\mathrm{R}}^{[Iv]} = A_{\mathrm{R}}(I,v)J_z^2 + B_{\mathrm{R}}(I,v)J_x^2 + C_{\mathrm{R}}(I,v)J_y^2 +$$

$$+ D_{\mathrm{R}}(I,v)J_y + E_{\mathrm{R}}(I,v)\{J_x, J_z\} + F_{\mathrm{R}}(I,v), \quad (49)$$

where

$$A_{\mathrm{R}}(I,v) = < b_+(\rho_1\rho_2) >_I < a(z) >_v +$$

$$+ < b_{12}(\rho_1\rho_2) >_I < a(z) >_v;$$

$$B_{\mathrm{R}}(I,v) = [< b_+(\rho_1\rho_2) >_I - < b_{12}(\rho_1\rho_2) >_I] < b(z) >_v;$$

$$C_{\mathrm{R}}(I,v) = c[< b_+(\rho_1\rho_2) >_I + < b_{12}(\rho_1\rho_2) >_I < z >_v];$$

$$D_{\mathrm{R}}(I,v) = \frac{1}{2} < b_-(\rho_1\rho_2) >_I < \left\{ (1-z^2)^{1/2}, p_z \right\} >_v -$$

$$- < G >_I < (1-z^2)^{1/2} >_v;$$

$$E_{\mathrm{R}}(I) = -\frac{1}{2} < b_-(\rho_1\rho_2) >_I;$$

$$F_{\mathrm{R}}(I,v) = < p_1^2 + p_2^2 >_I + 2b_0 < p_1p_2 >_I < z >_v +$$

$$+ < b_+(\rho_1\rho_2) >_I < p_z(1-z^2)p_z >_v +$$

$$+ \frac{1}{2} < b_{12}(\rho_1\rho_2) >_I < \{z, p_z(z^2-1)p_z\} >_v +$$

$$+ < G >_I < \{1-z^2, p_z\} >.$$

The first three terms, obviously, determine the main part of the operator $\tilde{H}_{\mathrm{R}}^{[Iv]}$, that describes the most part of the rotational energy. They represent the asymmetric-top Hamiltonian with I- and v-dependent rotational constants. The analysis, analogous to the previous one, shows that the other terms give the vibrational energy with small corrections caused by the interaction of rotation with the stretching and bending oscillations.

Consider an iteration of the simulation of high-excited rotational states. Using the symmetric-top approximation (25) and the model wave functions (29) and (48), as well as Eqs. (44)–(45) for Eq. (49), we obtain

$$A_{\mathrm{R}}(I,v) = \frac{b_0N_v^2}{2} \int_{-1}^{1} (1-z)^{\alpha_0} (1+z)^{\sqrt{\beta_0^2+k^2(1+C_b)}-1} \times$$

$$\times \left(P_v^{(\alpha_0, \sqrt{\beta_0^2+k^2(1+C_b)}-1)} \right)^2 \mathrm{d}z \left\{ R_{nm}(-2) + R_{mm}(-2) + \right.$$

$$\left. + 2\sigma\delta_{nm}R_{nm}(-2) + 2\left(R_{nn}(-1)R_{mm}(-1) + \sigma R_{nm}^2(-1) \right) \right\};$$

$$B_{\mathrm{R}}(I,v) = \frac{b_0N_v^2}{2} \int_{-1}^{1} (1-z)^{\alpha_0-1} (1+z)^{\sqrt{\beta_0^2+k^2(1+C_b)}} \times$$

$$\times \left(P_v^{(\alpha_0-1, \sqrt{\beta_0^2+k^2(1+C_b)})} \right)^2 \mathrm{d}z \left\{ R_{nm}(-2) + R_{mm}(-2) + \right.$$

$$\left. + 2\sigma\delta_{nm}R_{nm}(-2) - 2\left(R_{nn}(-1)R_{mm}(-1) + \sigma R_{nm}^2(-1) \right) \right\};$$

$$C_{\mathrm{R}}(I,v) = \frac{b_0N_v^2}{4} \int_{-1}^{1} z(1-z)^{\alpha_0} (1+z)^{\sqrt{\beta_0^2+k^2(1+C_b)}} \times$$

$$\times \left(P_v^{(\alpha_0, \sqrt{\beta_0^2+k^2(1+C_b)})} \right)^2 \mathrm{d}z \left\{ R_{nm}(-2) + R_{mm}(-2) + \right.$$

$$\left. + 2\sigma\delta_{nm}R_{nm}(-2) + 2\left(R_{nn}(-1)R_{mm}(-1) + \sigma R_{nm}^2(-1) \right) \right\},$$

where

$$R_{nm}(\rho) = r_{\mathrm{e}} \int_0^{\infty} S_n(\rho)S_m(\rho)\rho^p \mathrm{d}\rho;$$

$$S_n(\rho) = N_n \rho^j e^{-\frac{\rho}{2}} L_n^{(2j+1)}(\rho);$$

$$C_b = \frac{< b_{12}(\rho_1\rho_2) >_I}{< b_+(\rho_1\rho_2) >_I}.$$

As an example, let us consider now the bending states of the H_2O molecule. Using the wave functions of rigid asymmetric top (rotational constants A, B, and C of the lower vibrational state of H_2O are taken from Ref. 10), we have calculated the average values of the squared projection of angular momentum $<J_\alpha^2>_r$. Figures 1 and 2 show these average values for the quantum numbers $J = 4$ and 20.

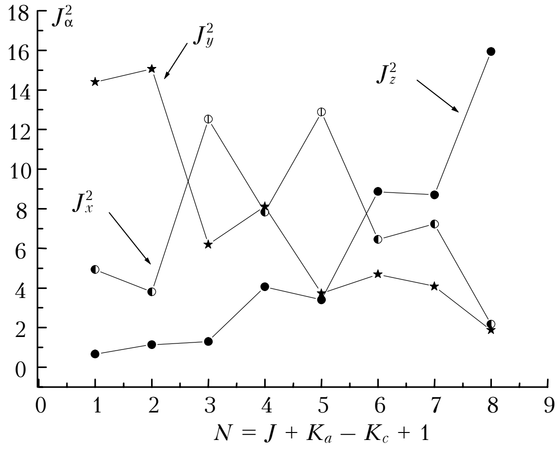

Fig. 1. Average values $<J_\alpha^2>_r$, $\alpha = x, y, z$ at $J = 4$.

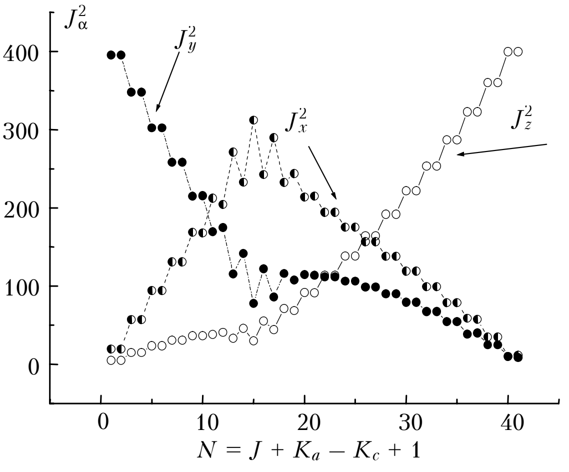

Fig. 2. Average values $<J_\alpha^2>_r$, $\alpha = x, y, z$ at $J = 20$.

As can be seen from Figs. 1 and 2, the average values of the squared components of the angular momentum vary very widely. Thus, for example, the average value $<J_z^2>_r$ increases 400 times as K_a increases from 0 to 20, while $<J_x^2>_r$ decreases from 400 to 10. It is obvious that these average values determine the model wave function (48) and affect the effective mean configuration and the probability density distribution.

The change of the wave function of the "effective" equations (14) reflects the change of the total wave functions at a high rotational excitation. The wave functions of the bending vibration for $J = 10$, 20, and 40 are shown in Figs. 3–5.

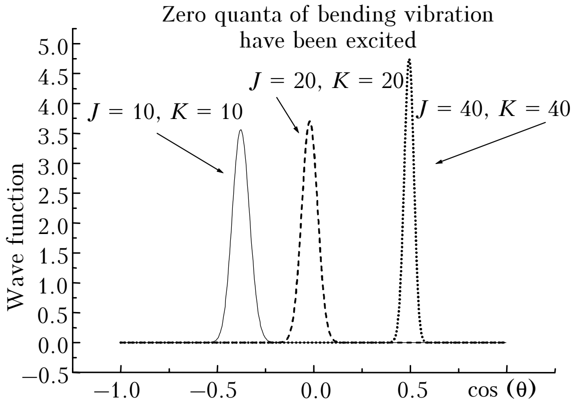

Fig. 3.

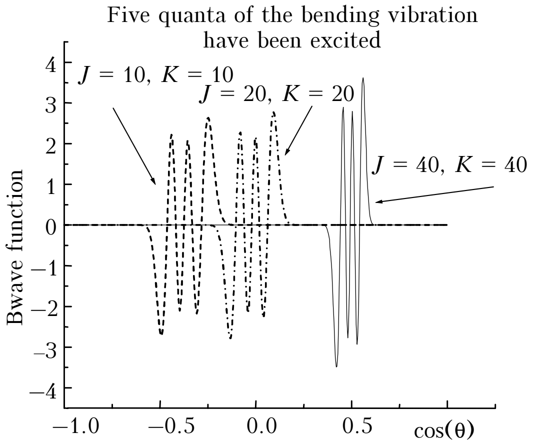

Fig. 4.

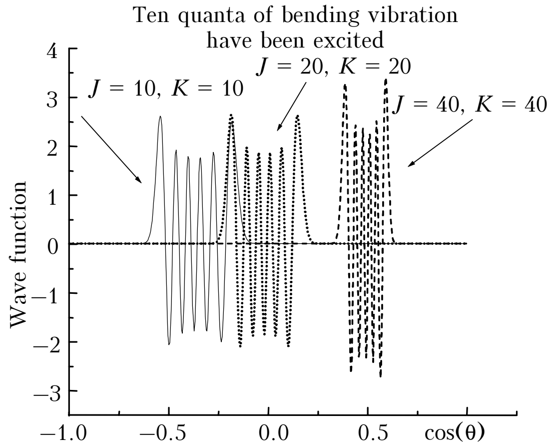

Fig. 5.

It should be noted that the area of localization of the bending wave functions shifts considerably to higher values of the variable $z = \cos(\theta)$ and the value of this shift appears to be practically the same for the wave functions with $v = 0$, 5, and 10. The wave functions become deformed, namely, compressed. The shift and deformation of the wave functions are caused by the complex character of the vibrational-rotational interaction in the water molecule and by the appearance of centrifugal addition to the effective potential energy function. Analogous additions, obviously, arise in the equations, describing the stretching vibrations as well [see Eqs. (28) and (29)].

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References

1. S. Carter and N.C. Handy, Comput. Phys. Rep. **5**, 115–172 (1986).
2. D. Papoušek and M.R. Aliev, *Molecular Vibrational-Rotational Spectra* (Elsevier, Amsterdam, 1982), 323 pp.
3. H.Y. Mussa and J. Tennyson, J. Chem. Phys. **109**, No. 24, 10885–10892 (1998).
4. M. Chaild and L. Halonen, Adv. Chem. Phys. **51**, No. 1, 1–58 (1984).
5. M. Chaild, O. Naumenko, and L. Brown, Mol. Phys. **92**, 885–893 (1997).
6. M. Chaild, T. Weston, and J. Tennyson, Mol. Phys. **96**, 371–379 (1999).
7. J. Makarewicz, J. Mol. Spectrosc. **130**, 316–336 (1988).
8. J. Makarewicz, J. Phys. B **21**, 3633–3651 (1988).
9. M.N. Nounkonnou, K. Soloda, Y. Justum, and D. Lauvergnat, J. Phys. B **37**, 1859–1872 (2004).
10. A.D. Bykov, B.A. Voronin, and S.S. Voronina, Atmos. Oceanic Opt. **15**, No. 12, 953–957 (2002).
11. J. Makarewicz, J. Phys. B **21**, 1803–1819 (1988).