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Exact solvable quantum models of rotating–vibrating triatomic molecules

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Abstract. Quantum models of rotating–vibrating triatomic molecules are presented. They are specified by model potential functions written in local or collective internal coordinates. For these models the exact rovibrational (rv) wavefunctions and energy levels are calculated for low values of the angular momentum quantum number J . For some states with high J approximate analytic formulae for energy levels are given. The proposed models are realistic and describe correctly the main features of rv states. New physical effects which occur in molecules due to strong rotation–vibration interaction are discussed.

1. Introduction

A good physical model is worth as much as a good theory. This fact has been confirmed by a commonly known model of the hydrogen atom, without which the theory of electronic states of atoms and molecules would not have been conceived. So far, there has not been such a universal and simple model for the theory of rv states.

The familiar normal-mode picture of molecular vibrations developed for semi-rigid molecules (see the monograph of Wilson *et al* 1955) is not universal since it is valid only for small-amplitude harmonic vibrations. Furthermore, it neglects completely the molecule rotations, which must be treated within the perturbation theory.

Useful theoretical models of another kind, describing the high-frequency stretching vibrations, are local-mode models. They give closer representation of the highly excited stretching modes than the traditional picture of multiple excitations of normal modes. A good discussion of the local-mode models is given in the review of Child and Halonen (1984).

The studies of the rotation–vibration interactions require more realistic models that could also describe molecule rotations. A good model of such a kind for a triatomic molecule was proposed some years ago by Hougen *et al* (1970). In their model the bond lengths were fixed; however the large-amplitude bending motion and overall rotations were taken into account. Such a reduced dynamic model proved very fruitful and has been further developed by other authors (for a review, see Bunker 1983). However, the calculation of rv wavefunctions and energy levels within the framework of the considered model requires advanced numerical techniques to be used.

A model of a triatomic molecule may play a similar role in the theory of rv states of polyatomic molecules to the hydrogen atom model in the theory of electronic states of many-electron systems. However, the triatomic rv problem is nothing more than

a three-body problem not solved until now. Here, we do not try to solve it generally but rather we look for realistic model potential functions describing the three-body interactions in the qualitatively correct way for which this problem can be solved exactly.

In this paper we present such models for a description of RV states of triatomic molecules. In § 2 we consider the reduced dynamic model with frozen stretching modes. The RV Hamiltonian of our model describing the bending and rotation molecule motions is analogous to the Hamiltonian of Hougen *et al* (1970). However, we use Radau's coordinates which allow us to simplify the form of the kinetic energy operator. Due to this fact we are able to solve analytically a four-dimensional bending-rotation problem for a realistic model potential function, which can describe linear or bent molecules. The exact solutions have been found only for RV states with low J . However, we also propose a very simple method for approximate calculations of quite accurate wavefunctions and energy levels even for some RV states with high J .

In § 3 the derived formulae are applied to typical linear and bent molecules. We prove that the main features of the RV energy spectrum are described correctly.

In § 4 we consider a six-dimensional RV problem including the stretching vibrations. By neglecting a small Coriolis term we are able to solve exactly the model problem describing all RV degrees of freedom. The stretching vibrations are treated as local modes.

In § 5 we solve a six-dimensional problem in terms of collective hyperspherical coordinates describing the symmetric and antisymmetric stretching vibrations.

The local and collective models are compared in § 6 and the results of the work are summarised in § 7.

2. Solution of the bending-rotation problem

In a triatomic molecule the coupling between the bending vibration and overall rotation is very important, since the bending vibration usually has a large amplitude. Thus, simplified models of a molecule which exhibits only the bending and rotation motions with frozen bond lengths are very useful in understanding the molecule dynamics.

Here, we will consider a model of this kind formulated in terms of Radau's coordinates: r_1 , r_2 and ϑ describing the internal molecule motions (for the definition of these coordinates, see e.g. Johnson and Reinhardt (1986)). These coordinates are very similar to the widely used valence coordinates \tilde{r}_1 , \tilde{r}_2 (bond lengths) and $\tilde{\vartheta}$ (bond angle) if the mass of the central atom (m_c) is much greater than the masses of terminal atoms (m_t) of a molecule. We will further consider only a water-like symmetric triatomic molecule with two identical terminal atoms, i.e. $m_1 = m_2 = m$.

The rotations of a molecule in an external space can be described by Euler angles $\phi = (\varphi, \theta, \chi)$. They define the orientation of a molecule-fixed (MF) axis system with respect to a laboratory space-fixed axis system. Here we use the following MF axes: the y axis lies in the molecule plane and bisects the internal angle ϑ ; the z axis also lies in the molecule plane and is perpendicular to the y axis; the x axis is perpendicular to the y and z axes and is chosen in such a way that the (x, y, z) -axis system is right handed.

The RV Hamiltonian $H(r_1, r_2, \vartheta, \phi)$ of a triatomic molecule, expressed in Radau's internal coordinates and Euler angles as external coordinates has been recently derived by the author (Makarewicz (1988a)); we will further cite the equations from that paper writing their numbers prefixed by I).

Now, let us consider the bending-rotation model Hamiltonian $H_{br}(\vartheta, \phi)$ which is obtained directly from the total Hamiltonian of equations (I 42-45) by fixing the coordinates r_k , i.e. $r_1 = r_2 = r_e$:

$$H_{br}(\vartheta, \phi) = B_e \Lambda_+^2(\vartheta, \phi) + U_b(\vartheta) \quad (1)$$

where

$$B_e \equiv 1/mr_e^2 \quad (2)$$

and $U_b(\vartheta)$ is the bending potential function. $\Lambda_+^2(\vartheta, \phi)$, defined in equation (I 44), has the physical meaning of a generalised four-dimensional angular momentum operator.

The Schrödinger equation for the rv wavefunction $\psi_{rv}(\vartheta, \phi)$

$$[H_{br}(\vartheta, \phi) - E_{rv}] \psi_{rv}(\vartheta, \phi) = 0 \quad (3)$$

can be written as

$$\left(h_{vib}(\vartheta) + (1/2) \sum_i \mu_i(\vartheta) J_i^2 - \mathcal{E}_{rv} \right) \psi_{rv}(\vartheta, \phi) = 0 \quad (4)$$

where

$$h_{vib}(\vartheta) = \Lambda_2^2(\vartheta) + V_b(\vartheta) \quad V_b \equiv U_b(\vartheta)/B_e \quad (5)$$

$$\mu_1 = \frac{1}{2} \quad \mu_2 = 1/(1 - \cos \vartheta) \quad \mu_3 = 1/(1 + \cos \vartheta) \quad (6)$$

and

$$E_{rv} = B_e \mathcal{E}_{rv}. \quad (7)$$

$(J_1, J_2, J_3) \equiv (J_x, J_y, J_z)$ are the angular momentum operators with respect to the MF axis system.

$\Lambda_2^2(\vartheta)$ is the special case of the operator

$$\Lambda_n^2(x) \equiv -\hbar^2 [\partial^2 / \partial x^2 + (n-1) \cot x \partial / \partial x] \quad (8)$$

which for small x has the same form as a radial part of the n -dimensional Laplacian (multiplied by $-\hbar^2$), namely

$$\Lambda_n^2(x) \approx \mathcal{D}_n^2(x) \equiv -\hbar^2 [\partial^2 / \partial x^2 + (n-1)x^{-1} \partial / \partial x]. \quad (9)$$

Equation (4) reflects the fact that the bending and rotation molecule motions cannot be considered separately.

Recently, it has been proved that the equation of a general form of equation (4) has separable solutions for several classes of rv states with low values of J (Makarewicz 1987a). These solutions can be written as

$$\psi_{rv}(\vartheta, \phi) = \Theta_v(\vartheta) \Phi_r(\phi) \quad (10)$$

where the rotational wavefunction $\Phi_r(\phi)$ depends only on the Euler angles and satisfies the equation

$$\left((1/2) \sum_i \mu_i(\vartheta) J_i^2 - \mathcal{E}_r(\vartheta) \right) \Phi_r(\phi) = 0 \quad (11)$$

where $\mathcal{E}_r(\vartheta)$ has the meaning of a rotational energy parametrically dependent on ϑ :

$$\mathcal{E}_r(\vartheta) = (1/2) \sum_i \mu_i(\vartheta) \lambda_i. \quad (12)$$

The constants λ_i depend on rotational quantum numbers because they are equal to expectation values $\langle J_i^2 \rangle$.

$\Phi_r(\phi)$ is the wavefunction in the form given by Wang (1929):

$$\Phi_r^{(J, K^\pm)} = 2^{-1/2}(|J, K\rangle \pm |J, -K\rangle) \quad \text{for} \quad K = 1, \dots, J$$

and

$$\Phi_r^{(J, 0)} = |J, 0\rangle$$

where $|J, \pm K\rangle$ is the symmetric-top wavefunction characterised by the quantum number K measuring the projection of the angular momentum on the MF z axis (Townes and Schawlow 1955). For the separable states

$$(J, K^\pm) = (1, 0), (1, 1^-), (1, 1^+), (2, 1^-), (2, 1^+), (2, 2^-), (3, 2^-)$$

the constants $(\lambda_1, \lambda_2, \lambda_3)$ are

$$(1, 1, 0), (1, 0, 1), (0, 1, 1), (4, 1, 1), (1, 4, 1), (1, 1, 4), (4, 4, 4)$$

respectively.

The symbol (J, K^\pm) will also be used for the identification of the non-separable states, although K is only an approximate quantum number for such states.

Substituting $\psi_{rv}(\vartheta, \phi)$ into (4) and taking into account equation (11) we come to the equation determining $\Theta_v(\vartheta)$:

$$[\Lambda_2^2(\vartheta) + V_{rb}(\vartheta) - \mathcal{E}_{rv}] \Theta_v(\vartheta) = 0 \quad (13)$$

where

$$V_{rb}(\vartheta) \equiv V_b(\vartheta) + \mathcal{E}_r(\vartheta) \quad (14)$$

is the effective potential including $\mathcal{E}_r(\vartheta)$ which plays the role of a centrifugal potential.

Now we find exact solutions of equation (13) for the following model potential function:

$$V_b(\vartheta) = V_-/[2(1 - \cos \vartheta)] + V_+[2(1 + \cos \vartheta)] - V_0 \quad (15)$$

where, for $\vartheta = \vartheta_e$, $V_b(\vartheta)$ approaches a minimum equal to $V_0 = V_b(\vartheta_e)$.

Introducing a more convenient variable, $t = \cos \vartheta$, we transform equation (13) to

$$\{L^2(t) + u_2/[2(1 - t)] + u_3/[2(1 + t)] - \varepsilon_{rv}\} \Theta_v(t) = 0 \quad (16)$$

where

$$\begin{aligned} L^2(t) &\equiv \partial/\partial t(t^2 - 1)\partial/\partial t \\ u_2 &\equiv (\lambda_2 + V_-)/\hbar^2 \quad u_3 \equiv (\lambda_3 + V_+)/\hbar^2 \end{aligned} \quad (17)$$

and

$$\mathcal{E}_{rv} = \hbar^2 \varepsilon_{rv} + \lambda_1/4 - V_0. \quad (18)$$

Since equation (16) has two singular points at $t = -1$ and $t = 1$ we will search for $\Theta_v(t)$ in the form

$$\Theta_v(\vartheta) = (1 - t)^{\alpha/2} (1 + t)^{\beta/2} P(t). \quad (19)$$

Choosing $\alpha = u_2^{1/2}$ and $\beta = u_3^{1/2}$, and introducing $\alpha_\pm \equiv (\alpha \pm \beta)/2$ we obtain the following equation for $P(t)$:

$$\{(t^2 - 1)\partial^2/\partial t^2 + 2[(\alpha_+ + 1)t + \alpha_-]\partial/\partial t + \alpha_+(\alpha_+ + 1) - \varepsilon_{rv}\} P(t) = 0. \quad (20)$$

This equation has the same form as that recently derived for the doubly excited helium atom (Makarewicz 1987b, equation (14)) and has the solutions: $P(t) = P_v^{(\alpha, \beta)}(t) =$ the Jacobi polynomial (Abramowitz and Stegun 1964, table 22.6) and

$$\varepsilon_{rv} = \nu(\nu + 1) \quad (21)$$

where

$$\nu \equiv v + \alpha_+.$$

Although the equations for helium and for a triatomic molecule are formally identical, they are physically not equivalent: the latter is more general. The equation for the helium was derived from three assumptions:

- (i) the internal coordinates are the valence coordinates;
- (ii) the mass of the central particle (nucleus) is infinite;
- (iii) the potential has a minimum at the linear configuration.

Here, instead of valence coordinates, we use Radau's coordinates which allow us to avoid the assumption (ii). Here, the condition (iii) is unnecessary since the potential (15) can be used to describe *non-linear* molecules. If $V_+ \neq 0$ then $V_b(t)$ approaches a minimum at $\vartheta \neq \pi$. $V_b(t)$ can also describe *linear* molecules because for $V_+ = 0$ it approaches a minimum at $\vartheta = \pi$.

Let us note that $\hbar^2 \varepsilon_{rv}$ resembles the eigenvalue $\hbar^2 l(l+1)$ of the three-dimensional angular momentum operator. This analogy has a deep physical sense because equation (16) describes all angular molecule motions, namely the external (overall) rotations and the angular internal motion which can be considered as an internal rotation hindered by the potential $V_b(t)$.

The solutions obtained are valid only for separable rv states. However, we can also calculate approximate, but nevertheless quite accurate, analytical solutions even for high values of J .

For high J and $K \approx 0$ a molecule rotates nearly about the MF x axis and then $K_c = J, J-1, \dots$ which measures the projection of the angular momentum on the MF x axis is approximately a good quantum number. For high K_c (low K) $\langle J_1^2 \rangle \approx (\hbar K_c)^2$.

When K is high it is a good quantum number (it equals the familiar K_a (Townes and Schawlow 1955)) and then $\langle J_3^2 \rangle \approx (\hbar K_a)^2$.

Recently it has been shown that the rv wavefunctions of the states from both regimes of a low and high K are almost separable and the approximate rotational wavefunction is similar to the symmetric-top wavefunction (Makarewicz 1988b). This is a consequence of the fact that in the considered regimes the asymmetric rotor reveals the features of a symmetric rotor, for example the levels (J, K^+) and (J, K^-) are practically degenerate. The origin of this degeneracy has recently been explained in the illuminating paper by Harter and Patterson (1984). Thus for the states with $K \approx 0$ we can take

$$\lambda_1 \approx (\hbar K_c)^2 \quad \lambda_2 \approx \lambda_3 \approx [J(J+1) - K_c^2] \hbar^2 / 2 \quad (22a)$$

and for $K \approx J$ we can take

$$\lambda_3 \approx (\hbar K_a)^2 \quad \lambda_1 \approx \lambda_2 \approx [J(J+1) - K_a^2] \hbar^2 / 2 \quad (22b)$$

and solve equation (16).

Such an approximation for intermediate values of K is not good and we propose another simple method for solving the rv problem. Let us first solve equation (16)

for λ_i defined in equation (22a) or (22b). Having found ε_{rv} we can easily calculate the expectation values

$$\langle \mu_i \rangle \equiv \int |\Theta_v(t)|^2 \mu_i(t) dt \left(\int |\Theta_v(t)|^2 dt \right)^{-1}.$$

Indeed, applying the Hellman-Feynman theorem (Hellmann 1937, Feynman 1939) to equation (16) we obtain

$$\langle \mu_i \rangle = 2\partial \varepsilon_{rv} / \partial u_i \quad \text{for} \quad i = 2, 3$$

and taking into account equation (21) we have

$$\langle \mu_2 \rangle = (2\nu + 1)/2\alpha \quad \langle \mu_3 \rangle = (2\nu + 1)/2\beta \quad (23)$$

and $\langle \mu_1 \rangle = \frac{1}{2}$; see equation (6).

These values can be used to calculate the rotational constants

$$B_i \equiv B_e \langle \mu_i \rangle / 2 \quad (B_1, B_2, B_3) \equiv (B_x, B_y, B_z) \quad (24)$$

which determine the effective rotational Hamiltonian

$$h_{\text{rot}} = \sum_i B_i J_i^2. \quad (25)$$

Its eigenvalues \tilde{E}_r for $J \leq 12$ can be easily calculated analytically (Townes and Schawlow 1955, table 4.1 and appendix III). Using the Hellman-Feynman theorem we can directly determine $\langle J_i^2 \rangle$ because

$$\langle J_i^2 \rangle = \lambda_i = \partial \tilde{E}_r / \partial B_i. \quad (26)$$

The calculated values λ_i are then substituted into equation (16) (see also (17)) and this equation gives approximate but very accurate rv energy levels. For example, the errors of such calculated rv energies for low v and J are of the order of $10^{-2}\%$ or lower. Thus, we are able to calculate analytically the exact or approximate rv energy levels and wavefunctions for all states (J, K^\pm) except when J is high and K is not too low or not too high (then neither K_a nor K_c are good quantum numbers).

In order to apply the derived formulae to calculate the rv energy levels of a given molecule we should estimate the potential parameters V_- and V_+ .

If the molecule is linear we need only one parameter, V_- , which can be determined from the fit of the calculated energy levels to the experimental ones. For our purposes we propose the simplest possible procedure. Namely, let us choose two vibrational states ($J=0$) with quantum numbers v and v' for which $\Delta E^{\text{expt}}(v', v) \equiv E_{rv'}^{\text{expt}} - E_{rv}^{\text{expt}}$ is known. Then, from the condition

$$\Delta E^{\text{expt}}(v', v) = E_{rv'}^{\text{calc}} - E_{rv}^{\text{calc}} \quad (27)$$

and equations (9, 17, 18, 21) we obtain:

$$V_- = [\Delta \mathcal{E}(v', v) - v' - v - 1]^2 \quad (28)$$

where

$$\Delta \mathcal{E}(v', v) \equiv \Delta E^{\text{expt}}(v', v) / [\hbar^2 B_e (v' - v)].$$

For a non-linear molecule we can use (27) and the additional condition, namely

$$\vartheta_e^{\text{expt}} = \vartheta_e^{\text{calc}}$$

where ϑ_e is the equilibrium value of ϑ . By comparing $\vartheta_e^{\text{expt}}$ determined experimentally with $\vartheta_e^{\text{calc}}$ calculated from

$$dV_b(\vartheta)/d\vartheta = 0$$

we come to

$$V_- = [(\Delta\mathcal{E}(v', v) - v' - v - 1)/(1 + c_e)]^2 \quad (29)$$

$$V_+ = c_e^2 V_- \quad (30)$$

where

$$c_e \equiv (1 + \cos \vartheta_e^{\text{expt}})/(1 - \cos \vartheta_e^{\text{expt}}).$$

Since we work with Radau's coordinates, we must remember that ϑ_e and r_e are not the equilibrium bond angle $\tilde{\vartheta}_e$ and bond length \tilde{r}_e , respectively. These quantities are related to ϑ_e and r_e by

$$\vartheta_e = 2 \tan^{-1}[\tilde{m}^{-1/2} \tan(\tilde{\vartheta}_e/2)] \quad (31)$$

$$r_e = \tilde{r}_e [\sin^2(\tilde{\vartheta}_e/2) + \tilde{m} \cos^2(\tilde{\vartheta}_e/2)]^{1/2} \quad \text{where} \quad \tilde{m} \equiv m_c/(m_c + 2m).$$

Knowing the experimentally determined parameters $\tilde{\vartheta}_e^{\text{expt}}$ and $\tilde{r}_e^{\text{expt}}$ we should first 'translate' them according to (31) into $\vartheta_e^{\text{expt}}$ and r_e^{expt} , and then use equations (28) or (29, 30). Naturally, the value of B_e in these equations should be calculated for $r_e = r_e^{\text{expt}}$ (see equation (2)).

The determined parameters V_- and V_+ can be applied to calculate the energy levels of a series of RV states with $J \neq 0$. This allows us to check if the model potential $V_b(\vartheta)$ is realistic.

3. The bending-rotation states of linear and bent molecules

Here we will apply the formulae from the previous section to calculate the RV energy levels and wavefunctions of some typical linear and bent triatomic molecules. The experimental equilibrium geometry parameters and also the parameters of the potential functions (determined by us) for triatomic molecules considered in this work are collected in table 1.

Table 2 contains the energy levels of the bending motion of the H_2O^+ molecule (in the \tilde{A}^2A_1 electronic state), calculated for the potential function $V_b(\vartheta)$ of equation (15) with $V_+ = 0$ (H_2O^+ has a linear equilibrium configuration). The parameter V_- has been determined from equation (28) by using $v = 2$ (the lowest observed energy level) and $v' = 7$ (the highest observed energy level). We can see that the transition energies $G_v \equiv \Delta E(v+1, v)$ are reproduced quite accurately. The errors of G_v are less than 3%. For comparison the G_v calculated numerically by Jungen *et al* (1980) are also presented in the table. Their G_v are more accurate than ours; however they have been calculated for a three-parameter potential function fitted to all observed transition energies.

In table 3 the RV energy levels of the C_3 molecule (in its $\tilde{X}^1\Sigma_g^+$ electronic state) are shown. We can see that the results obtained as for H_2O^+ have the same quality as the results of Kraemer *et al* (1984) calculated by very sophisticated numerical methods. Our results are reasonable, although they are significantly worse than the numerical results of Jungen and Merer (1980) calculated for a three-parameter potential

Table 1. Equilibrium values of the valence coordinates \tilde{r}_e (in Å) and $\tilde{\vartheta}_e$ (in degrees), and potential parameters (in cm^{-1}) of the model Hamiltonians for the molecules considered in this work.

The bending-rotation Hamiltonian			
Molecule:	C_e^a	$(\text{H}_2\text{O}^+)^b$	H_2O^c
\tilde{r}_e	1.299	0.997	0.9740
$\tilde{\vartheta}_e$	180	180	104.62
V_-	232 490	82 395	22 900
V_+	0	0	6 437
The stretching-bending-rotation Hamiltonian of H_2O			
	Local model	Collective model	
\tilde{r}_e	0.9572 ^d	0.9572 ^d	
$\tilde{\vartheta}_e$	104.62	104.62	
V_-	11 190	22 220	
V_+	3 146	6 247	
D_e	187 500	369 700	
A	—	83 300	

^a \tilde{r}_e and $\tilde{\vartheta}_e$ have been determined by Jungen and Merer (1980).

^b \tilde{r}_e and $\tilde{\vartheta}_e$ have been determined by Jungen *et al* (1980).

^c \tilde{r}_e and $\tilde{\vartheta}_e$ have been determined by Bunker and Landsberg (1977).

^d \tilde{r}_e and $\tilde{\vartheta}_e$ have been determined by Hoy *et al* (1972).

Table 2. Comparison of the observed and calculated transition energies $G_v = \Delta E(v+1, v)$ (in cm^{-1}) for the bending mode of the H_2O^+ molecule.

v	$G_v^{\text{obs } a}$	$G_v^{\text{calc } b}$	G_v^{calc} (this work)
0	—	0.0	0.0
1	—	1682.2	1731.1
2	—	1808.4	1798.4
3	1893.7	1896.3	1865.7
4	1960.6	1961.7	1933.0
5	2009.6	2012.0	2000.3
6	2056.2	2051.4	2067.6
7	2082.0	2082.4	2134.9

^a Lew (1976).

^b Jungen *et al* (1980).

function. The example of C_3 proves that Radau's coordinates are adequate also for molecules with heavy terminal atoms.

The rv energy levels of H_2O , which is bent in the equilibrium configuration, are shown in table 4. For determining the parameters V_- and V_+ we used $\Delta E^{\text{expt}}(v', v)$ for $v=0$ and $v'=2$. The calculated G_v increase with v , in contrast to the observed ones which decrease. For example $G_1^{\text{calc}} = 1541.3$ and $G_2^{\text{calc}} = 1614.9$ whereas $G_1^{\text{expt}} = 1594.8$ and $G_2^{\text{expt}} = 1561.5$ (G_v are in cm^{-1}). As follows from (21) the assumed form of $V_b(\vartheta)$ always gives increasing G_v so it can be used only for a rough estimation of

Table 3. Comparison of the observed and calculated bending-rotation energy levels $E(v, J, K^\pm)$ of the C_3 molecule. (J, v, K^\pm) are the quantum numbers used in the text and $\tilde{\nu}'$ is the symbol traditionally used for linear molecules; $\tilde{\nu} \equiv 2\nu + l$ and $l \equiv K$. $E(v, J, K^\pm)$ are given in cm^{-1} relative to the ground-state energy level $E(0, 0, 0)$.

J	v	K^\pm	$\tilde{\nu}'$	Obs. ^a	Calc. ^b	Calc. (this work)
0	0	0	0 ⁰	0.0	0.00	0.00
1	0	0	0 ⁰	—	0.87 ^c	0.84
1	0	1 ⁻	1 ¹	63.1	68.69 ^c	70.80
1	0	1 ⁺	1 ¹	—	68.70 ^c	70.81
0	1	0	2 ⁰	132.72	132.65	141.60
1	1	1 ⁻	3 ¹	206.98	207.22	214.06
0	2	2	4 ⁰	286.52	286.42	286.52
1	2	1 ⁻	5 ¹	—	370.21	360.65
0	3	0	6 ⁰	458.2 ^b	457.35	434.78

^a Gausset *et al* (1965).

^b Jungen and Merer (1980) unless otherwise stated.

^c Kraemer *et al* (1984).

Table 4. Comparison of the observed and calculated rotation-bending energy levels $E(v, J, K^\pm)$ of the H_2O molecule using $V_b(\vartheta)$ given in equation (26). $E(v, J, K^\pm)$ are given in cm^{-1} relative to the corresponding rotationless energy level $E(v, 0, 0)$.

v	J	K^\pm	0		1		2	
			Obs. ^a	Calc.	Obs. ^a	Calc.	Obs. ^a	Calc.
0	0		0.0	0.0	1594.7	1541.3	3156.2	3156.2
1	0		23.8	23.6	23.8	24.3	23.8	25.0
1	1 ⁻		37.1	36.4	40.2	37.7	44.5	39.1
1	1 ⁺		42.4	41.6	45.8	43.7	50.3	45.7
2	0		70.1	69.6	70.2	71.4	70.3	73.3
2	1 ⁻		79.5	78.5	82.3	80.5	86.3	82.5
2	1 ⁺		95.2	94.2	98.9	98.3	103.8	102.5
2	2 ⁻		134.9	132.2	147.6	138.2	164.7	144.2
2	2 ⁺		136.2	133.6	148.7	139.8	165.7	146.1
3	0		136.8	135.7	137.2	138.8	137.6	141.8
3	1 ⁻		142.3	140.8	144.8	143.7	148.4	146.7
3	1 ⁺		173.4	171.9	177.7	179.0	183.0	186.1
3	2 ⁻		206.3	203.2	219.0	211.3	236.2	219.5
3	2 ⁺		212.2	209.4	224.6	218.7	241.2	228.1
3	3 ⁻		285.2	279.5	312.7	292.6	349.3	305.7
3	3 ⁺		285.4	279.8	312.9	292.9	349.4	306.1

^a Flaud and Camy-Peyret (1976).

the vibrational energies. Nevertheless, the predicted rotational energies for the lowest v are very close to the observed ones not only for low, but also for high J (see table 5). The quality of the results falls as v increases; however the main features of the rotational energy pattern are described correctly. For example, the K splittings of the levels $E(v, J, K^-)$ and $E(v, J, K^+)$ are estimated qualitatively well.

The results in table 5 indicate that the approximate expressions (22*a, b*) for λ_i are indeed correct for high J . The improvement of rv energy levels achieved by calculating

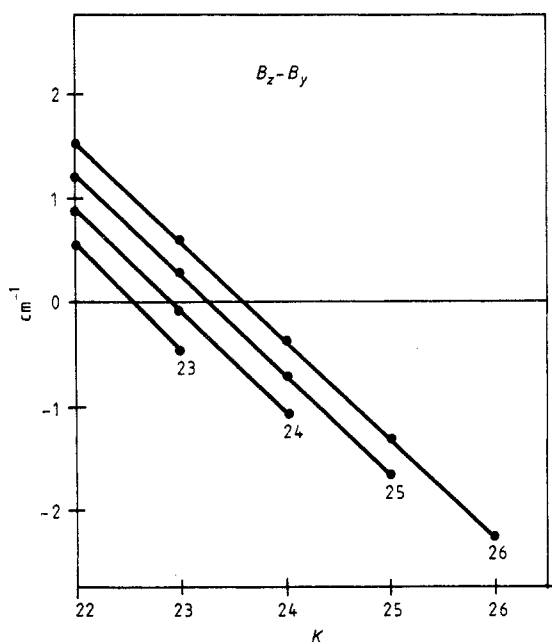
Table 5. Energy levels (in cm^{-1}) of H_2O in some RV states with $v = 0$ and $J = 10$, calculated with the use of approximate λ_i given in equations (22a, b) and (26).

K	8	9	10
Equation (22) λ_1	23.00	14.50	5.00
λ_2	23.00	14.50	5.00
λ_3	64.00	81.00	100.00
E	2219	2432	2657
Equation (26) λ_1	17.28	10.88	3.90
λ_2	30.22	19.18	6.53
λ_3	62.50	79.94	99.57
E	2238	2445	2660
E^{obs}^a	2254.3	2471.3	2701.9

^a Flaud and Camy-Peyret (1976).

more accurate values of λ_i (see equation (26)) is small. This fact supports our assumption that a bent molecule in states with low or high K for $J \gg 1$, can be treated as a symmetric top.

Studying highly excited rotational states of H_2O we have found a very interesting effect. In such states the centrifugal forces created by the rotations about the MF z axis are very strong and they can deform the molecule dramatically. This is evident from the fact that for sufficiently high $J > J^0$, where J^0 is some critical value of J , the hierarchy of the rotational constants is changed! For low K the rotational constant B_y is about two times smaller than B_z but B_y increases and simultaneously B_z diminishes

**Figure 1.** The difference $B_z - B_y$ calculated for H_2O in RV states with high J (the numbers under the curves) and high K ; $v = 2$.

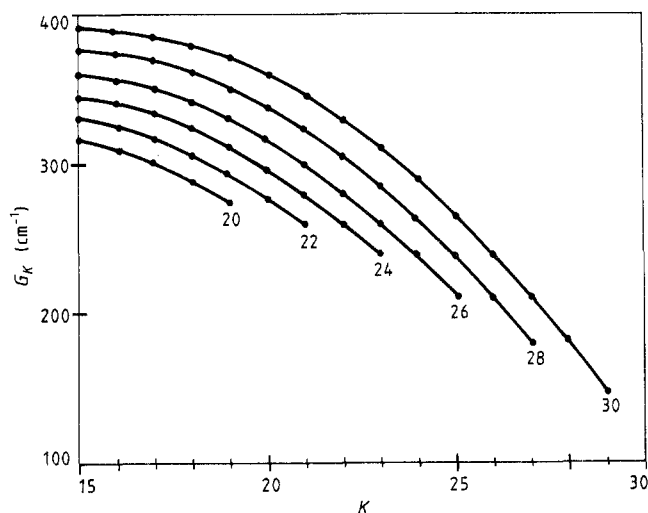


Figure 2. Rotational transition energies $G_K = E(v, J, K+1) - E(v, J, K)$ calculated for H_2O in RV states with high J (the numbers under the curves) and high K ; $v=2$. The splittings of the levels with K^- and K^+ are neglected.

as K increases. As a result, for some critical value of K (denoted by K^0) B_z becomes lower than B_y . The possibility of such an effect has recently been suggested (Makarewicz 1988b), but the calculations for $J > 20$ have not been performed.

For our model we obtain $J^0 = 23$ and K^0 which changes with $J > J^0$. The higher J , the more states with $K > K^0$ appear, e.g. for $J = J^0 = 23$ there is only one state with $K = K^0$, but for $J = 25$ there exist two states with $K \geq K^0 = 24$ (see figure 1). For $K > K^0$ the difference $B_z - B_y$ is quite small, so the molecular rotor is nearly symmetric with the MF x axis corresponding to the greatest moment of inertia. However, paradoxically, the K (defined with respect to the MF z axis; $K \equiv K_z$) is still a good quantum number, as if a molecule were a symmetric rotor with $B_x \approx B_y$. The dynamical interaction between the rotation and the bending motion changes the hierarchy of MF axes, but does not change the stable character of the MF z axis. Probably, for very high J and K this stability can be destroyed.

So far it has been assumed that the rotor properties are perturbed only by vibrations. However, we can see that the centrifugal deformations influence its properties to a considerably greater degree.

It is worthwhile noting that for high J and K the rotational energy pattern is qualitatively different from that for the rigid rotor (of prolate type), for which the rotational quanta increase with K . In contrast, the rotational quanta of a deformable rotor decrease because B_z which gives the greatest contribution to the rotational energy decreases with K . This fact is illustrated in figure 2.

4. Local-mode model of the stretching vibrations

The full RV problem including the stretching vibrations of a symmetric triatomic molecule can be reduced to simpler problems if we neglect the operator Λ_-^2 (see equation (145)) in the total RV Hamiltonian. For the model potential function of the

general form

$$V_L(r_1, r_2, \vartheta) = V_{12}(r_1, r_2) + (r_1^{-2} + r_2^{-2}) V_b(\vartheta) \quad (32)$$

the six-dimensional Schrödinger equation for the rv wavefunction $\Psi(r_1, r_2, \vartheta, \phi)$ can be separated into two equations of lower dimensions. The term $V_b(\vartheta)$ in (32) describing the potential of the hindered bending motion is damped at large distances by the factor $(r_1^{-2} + r_2^{-2})$. When $r_k \Rightarrow \infty$, $V_b(\vartheta)$ ceases to affect the bending motion and this should be expected in the real situation. Thus, the assumed potential function has a proper asymptotic behaviour.

The rv wavefunction can be factorised:

$$\Psi(r_1, r_2, \vartheta, \phi) = \mathcal{R}(r_1, r_2) \psi_{rv}(\vartheta, \phi) \quad (33)$$

and in order to solve the rv Schrödinger equation

$$[\tilde{H}(r_1, r_2, \vartheta, \phi) - E] \Psi(r_1, r_2, \vartheta, \phi) = 0 \quad (34)$$

where \tilde{H} does not include the operator Λ_-^2 , we first solve the equation determining $\psi_{rv}(\vartheta, \phi)$:

$$[\Lambda_+^2(\vartheta, \phi) + 2m V_b(\vartheta) - \mathcal{E}_{rv}] \psi_{rv}(\vartheta, \phi) = 0. \quad (35)$$

This equation has a similar form to equation (4) solved in § 2 and the eigenvalues \mathcal{E}_{rv} in (35) for $V_b(\vartheta)$ given by (15) can be calculated from (17, 18, 21); however, V_{\pm} in (17) (and V_0 in (18)) should be replaced by $2m V_{\pm}$ (and by $2m V_0$).

Now, substituting ψ_{rv} into (34) and taking (35) into account we come to the equation defining $\mathcal{R}(r_1, r_2)$:

$$\{[\mathcal{D}_3^2(r_1) + \mathcal{D}_3^2(r_2) + (r_1^{-2} + r_2^{-2}) \mathcal{E}_{rv}]/2m + V_{12}(r_1, r_2) - E\} \mathcal{R}(r_1, r_2) = 0. \quad (36)$$

Thus, we have reduced the six-dimensional equation (34) to a four-dimensional equation (35) and the two-dimensional equation (36). The last one can be further reduced if $V_{12}(r_1, r_2)$ is additive, i.e.

$$V_{12}(r_1, r_2) = V(r_1) + V(r_2).$$

It is well known that for many molecules such an additivity (assumed in local mode models) holds approximately. For an additive potential the function $\mathcal{R}(r_1, r_2)$ factorises into two components:

$$\mathcal{R}(r_1, r_2) = \mathcal{R}_1(r_1) \mathcal{R}_2(r_2) \quad (37)$$

and each $\mathcal{R}_k(r_k)$ fulfils

$$\{[\mathcal{D}_3^2(r_k) + r_k^{-2} \mathcal{E}_{rv}]/2m + V(r_k) - e_k\} \mathcal{R}_{v_k}(r_k) = 0 \quad k = 1, 2 \quad (38)$$

where

$$E = e_1 + e_2$$

and $\mathcal{D}_3^2(r)$ is defined in (9).

Let us note that if the stretching vibration quantum numbers v_1 and v_2 are different then for a symmetric molecule, $\mathcal{R}(r_1, r_2)$ has no defined symmetry with respect to the permutation of r_1 and r_2 . Then we must use the combinations

$$\mathcal{R}_{\pm}(r_1, r_2) = \mathcal{R}_{v_1}(r_1) \mathcal{R}_{v_2}(r_2) \pm \mathcal{R}_{v_1}(r_2) \mathcal{R}_{v_2}(r_1) \quad (39)$$

which have proper symmetry and also satisfy equation (38). We see that each energy level $E(v_1, v_2, v, J, K^{\pm})$ is twofold degenerate if $v_1 \neq v_2$. In real molecules this degeneracy is removed by non-additive potential energy terms.

Now, let us solve equation (38) for a reasonably chosen potential function $V(r_k)$. Usually, it is modelled by the Morse potential function; however, for this function the analytic solutions of equation (38) with the 'centrifugal' term $\mathcal{E}_{rv}/2mr_k^2$ are unknown. Recently, it has been recognised (Simons *et al* 1973) that for low excited states of the stretching modes the Kratzer (1920) potential

$$V(r) = D_e[1 - (r_e/r)]^2 \quad (40)$$

which has a minimum at $r = r_e$, reproduces satisfactorily the energies of the stretching modes. Let us emphasise that D_e should not be identified with the dissociation energy of a real molecule because the Kratzer potential approaches the dissociation limit too slowly. D_e should be treated only as a fitting parameter.

The advantage of this potential is that equation (38) has analytic solutions of the same form as those founded by Fues (1926). The eigenvalues e_k are given by

$$e_k = D_e[1 - d^2/(v_k + j_{rv} + 1)^2] \quad (41)$$

where

$$d^2 \equiv 2mD_e r_e^2 / \hbar^2 \quad (42)$$

and j_{rv} is calculated from

$$j_{rv} = (d^2 + \mathcal{E}_{rv}/\hbar^2 + \frac{1}{4})^{1/2} - \frac{1}{2}. \quad (43)$$

Using (41) and the Hellmann-Feynman theorem in equation (38) we obtain directly the expectation values

$$\langle r_k^{-2} \rangle = r_e^{-2} \delta_k^4 [1 - (v_k + \frac{1}{2})\delta_k/d]^{-1} \quad \delta_k \equiv 1 - e_k/D_e \quad (44)$$

which can be used to calculate the effective rotational constants:

$$B_i = (1/4m)[\langle r_1^{-2} \rangle_{v_1} + \langle r_2^{-2} \rangle_{v_2}]\langle \mu_i \rangle_v.$$

For completeness let us also write the eigenfunctions \mathcal{R}_{v_k} (Fues 1926):

$$\mathcal{R}_v(\tilde{r}) = N_v \tilde{r}^j \exp(-\tilde{r}/2) L_v^{(2j+1)}(\tilde{r}) \quad (45)$$

where $L_v^{(2j+1)}$ is the generalised Laguerre polynomial (Abramowitz and Stegun 1964, table 22.2) of the variable

$$\tilde{r} \equiv [2d/(v + j_{rv} + 1)](r/r_e).$$

Here, the indices k and rv are omitted.

5. Collective model of the stretching vibrations

The collective hyperspherical coordinates (see (I 47)) are defined by the hyperradius R and hyperangle ρ (which was denoted in I as α). $R(\rho)$ describes the symmetric (antisymmetric) stretching vibration of a molecule. In terms of these coordinates the six-dimensional rv Schrödinger equation without the operator Λ_-^2 can be separated for the potential

$$V(R, \rho, \vartheta) = V_s(R) + 2R^{-2}[V_a(\rho) + V_b(\vartheta)/\sin^2 \rho] \quad (46)$$

(here the constant 2 is introduced for convenience).

The wavefunction $\Psi(R, \rho, \vartheta, \phi)$ for the separable states can be factorised according to

$$\Psi(R, \alpha, \rho, \phi) = \mathcal{R}_s(R) \mathcal{G}_a(\rho) \psi_{rv}(\vartheta, \phi). \quad (47)$$

Taking into account the kinetic energy operator (given in (I 49, 50)) we can reduce the full RV problem to the following three equations. The first equation for ψ_{rv} is identical to equation (4) and the remaining two are

$$[\Lambda_3^2(\rho) + V_a(\rho) + \mathcal{E}_{rv}/\sin^2 \rho - \mathcal{E}_{rva}] \mathcal{G}_a(\rho) = 0 \quad (48)$$

$$\{\mathcal{D}_6^2(R) + 4\mathcal{E}_{rva}/R^2 + 2[V_s(R) - E]\} \mathcal{R}_s(R) = 0. \quad (49)$$

Let us solve equation (48) for the model potential function:

$$V_a(\rho) = A(1/\sin^2 \rho - 1). \quad (50)$$

The substitution

$$\mathcal{G}_a(\rho) = \mathcal{F}(\rho)/\sin \rho$$

transforms equation (48) to

$$[-\hbar^2 d^2/d\rho^2 + (A + \mathcal{E}_{rv})/\sin^2 \rho - (\mathcal{E}_{rva} + A + 1)] \mathcal{F}(\rho) = 0. \quad (51)$$

A similar equation can be found in the handbook of Abramowitz and Stegun (1964, table 22.6). The eigenvalues \mathcal{E}_{rva} are given by

$$\mathcal{E}_{rva} = \hbar^2(v_a + \gamma)^2 - A - 1 \quad \text{where} \quad v_a = 0, 1, 2, \dots \quad (52)$$

and γ is defined by

$$\hbar^2 \gamma(\gamma - 1) = A + \mathcal{E}_{rva},$$

which leads to

$$\gamma = \{[1 + (\mathcal{E}_{rva} + A)/(2\hbar^2)]^{1/2} + 1\}/2. \quad (53)$$

The eigenfunctions $\mathcal{F}_{v_a}(\rho)$ are expressed by Gegenbauer polynomials $\mathcal{C}_{v_a}^{(\gamma)}$ (see Abramowitz and Stegun 1964, table 22.2):

$$\mathcal{F}_{v_a}(\rho) = (\sin \rho)^\gamma \mathcal{C}_{v_a}^{(\gamma)}(\cos \rho). \quad (54)$$

Now we come to equation (49) which can also be solved for the model potential $V_s(R)$:

$$V_s(R) = D_e(1 - R_e/R)^2. \quad (55)$$

Writing $\mathcal{R}_s(R)$ as

$$\mathcal{R}_s(R) = R^{-3/2} \mathcal{S}(R)$$

we obtain the equation for $\mathcal{S}(R)$:

$$\{\mathcal{D}_3^2(R) + (15\hbar^2 + 16\mathcal{E}_{rva})/4R^2 + 2[D_e(1 - R_e/R)^2 - E]\} \mathcal{S}(R) = 0 \quad (56)$$

which has solutions analogous to those of equation (38). The eigenvalue $E(v_s, v_a, v, J, K^\pm)$ is given by formula (41) in which v_k , d and j_{rv} should be replaced by v_s (which is the quantum number of the symmetric stretching vibration), $d_e = 2D_e(R_e/\hbar)^2$ and

$$j_{rva} = (d_e^2 + 4 + 4\mathcal{E}_{rva}/\hbar^2)^{1/2} - \frac{1}{2}. \quad (57)$$

respectively.

6. Comparison of the local and collective models for H₂O

The spectrum of the stretching mode excitations in molecules like H₂O reveals a multiplet structure. The energy levels with the same sum $v_+ = v_1 + v_2$ of the stretching quantum numbers are grouped in multiplets. They are composed of doublets of close lying energy levels $(v_1, v_2)^+$ and $(v_1, v_2)^-$ corresponding to approximate wavefunctions (39).

In the simple local-mode (LM) model in which the interaction between two bond stretching vibrations is neglected the doublet splittings ΔE^\pm are zero. The data (for the ground state of the bending mode) collected in table 6 indicate that ΔE^\pm become very small for multiplets with high v_+ . The splitting of the lowest doublet in each multiplet is the smallest. However, in low multiplets the doublet splittings are not negligible.

Table 6. Comparison of the observed energy levels (in cm⁻¹) of the stretching modes of H₂O with those calculated for LM and CM models. v_1, v_2^\pm and v_s, v_a are the LM and CM quantum numbers, respectively. The differences between energies of neighbouring levels in multiplets are also given.

v_1, v_2^\pm	LM		Obs. ^a		CM		v_s, v_a
1 0 ⁺	3 657		3 657		6 657		1 0
1 0 ⁻	3 657	0	3 756	99	3 756	99	0 1
2 0 ⁺	7 207		7 202		7 260		2 0
2 0 ⁻	7 207	0	7 250	48	7 357	97	1 1
1 1 ⁺	7 314	107	7 445	195	7 507	150	0 2
3 0 ⁺	10 654		10 600		10 809		3 0
3 0 ⁻	10 654	0	10 613	14	10 905	96	2 1
2 1 ⁺	10 864	210	10 869	256	11 052	147	1 2
2 1 ⁻	10 864	0	11 032	164	11 251	199	0 3
4 0 ⁺	14 002		13 828		14 305		4 0
4 0 ⁻	14 002	0	13 831	3	14 399	94	3 1
3 1 ⁺	14 311	309	14 221	390	14 545	146	2 2
3 1 ⁻	14 311	0	14 319	98	14 741	196	1 3
2 2 ⁺	14 414	103	14 537	218	14 986	245	0 4

^a Data from compilation of Child and Lawton (1982); here those data are rounded to 1 cm⁻¹.

The collective-mode (CM) model based on hyperspherical coordinates describes the structure of low multiplets correctly (see table 6). However, ΔE^\pm for the lowest doublets in the multiplets are too large in this model.

Both models are compared in figure 3. The CM is better for low multiplets and LM is better for high multiplets.

The results of table 7 indicate that LM describes the rotational structure of high multiplets quite well, remembering how subtle the energy changes are which are taken into consideration. The total RV energy of the considered states (4, 1) and (3, 2) is about 17 000 cm⁻¹ whereas the difference of the rotational energies in these states is of the order of 10 cm⁻¹ or lower.

The stretching vibrations do not influence the centrifugal deformation, discussed in § 3, sufficiently. The calculated critical value J^0 for the lowest bending and stretching mode states of H₂O is 25. The critical values K^0 almost do not change with the stretching excitations, so the bending-rotation model in which the frozen bond lengths

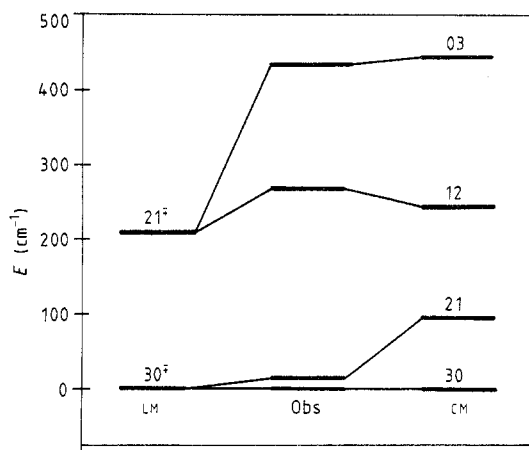


Figure 3. Comparison of the observed (Obs) energy levels of H₂O in the excited stretching states ($v_+ = 3$) with the calculated LM and CM energy levels. The energies are given relative to the lowest level in the multiplet.

Table 7. Differences in the rotational energies (in cm⁻¹) of H₂O in the states with five stretching quanta and those with no stretching quanta.

		$(v_1, v_2) = (3, 2)$		$(4, 1)$	
J	K^π	Obs. ^a	Calc.	Obs. ^a	Calc.
1	0	1.7	1.7	1.6	1.3
	1 ⁻	3.7	2.6	3.6	2.1
	1 ⁺	3.8	3.0	3.8	2.4
2	0	4.9	5.0	—	3.9
	1 ⁻	6.9	5.7	6.8	4.4
	1 ⁺	7.4	6.8	7.3	5.3
	2 ⁻	12.0	9.6	11.5	7.5
	2 ⁺	11.9	9.7	11.6	7.5
3	0	11.0	9.8	11.0	7.7
	1 ⁻	11.9	10.2	11.5	8.0
	1 ⁺	12.6	12.5	13.1	9.7
	2 ⁻	16.7	14.7	16.1	11.5
	2 ⁺	16.5	15.1	15.9	11.8
	3 ⁻	18.6	20.3	—	15.8
	3 ⁺	18.6	20.3	18.9	15.8

^a From data of Rothman (1978) and Antipov *et al* (1982).

are assumed, describes the centrifugal deformations of a molecule qualitatively correctly.

Using LM we have found an interesting phenomenon. This is a predissociation barrier generated by the vibrational bending motion. The rotational barrier is well known to occur in diatomic molecules (Herzberg 1950). In highly excited rotational states the centrifugal potential term can be so great that it can generate a potential barrier V_B at a distance $r_B > r_e$. Thus, tunnelling through such a barrier is possible.

For studying an analogous potential barrier in the H_2O molecule we considered the Morse potential function $V(r_k) = V_M(r_k)$ with the parameters $D_e = 44\,500\text{ cm}^{-1}$ and $a = 2.18\text{ \AA}^{-1}$ determined by Wallace (1975). This potential is more accurate near the dissociation limit than the Kratzer potential.

The effective potential $V_{\text{eff}}(r_k) \equiv V_M(r_k) + \mathcal{E}_{rv}/2mr_k^2$ for the stretching modes ($k = 1, 2$) can have a barrier for rotationless states if the bending mode is excited. The physical origin of this effect is clearly understandable. Since the bending vibration is a kind of angular motion it creates the centrifugal force. Let us note that the bending-rotation energy \mathcal{E}_{rv} modifying the stretching vibrations (see equation (38)) includes both rotational and bending contributions on an equal footing. It is interesting that the predissociation barrier occurs even in low excited bending-mode states and it grows with v faster than with J (see table 8). Probably a very complex rotational spectrum of some molecules, e.g. H_3^+ , in the high-energy regime is due to vibration-rotation predissociation.

Table 8. Height of the predissociation barrier V_B (in cm^{-1}) and its position r_B (in \AA) generated by the bending and rotation motions of H_2O . The results are obtained for the LM model.

	V_B	r_B		V_B	r_B
	$J = 0$			$v = 0$	
$v =$	5	167 4.43	$J = K =$	15	101 4.69
	10	489 3.92		20	185 4.37
	15	834 3.56		25	293 4.14
	20	1378 3.28		30	428 3.93

7. Summary

In this paper we presented models of triatomic molecules for which exact rv wavefunctions and energy levels have been found. The models are specified by the assumed potential function and kinetic energy operator. In the bending-rotation model the radial coordinates are fixed and due to this assumption the differential operators $\mathcal{D}_3^2(r_k)$ are eliminated. This model is similar to the 'rigid-bender' model of Hougen *et al* (1970).

The six-dimensional models including also the stretching vibrations are more realistic. The only simplification of the kinetic energy operator is the neglect of the operator Λ^2 . In such a case exact solutions exist for the rv states indicated in table 9. Let us note, however, that Λ^2 acting on the state $(1, 1^-)$ gives zero. Thus, this state is also exact if Λ^2 is included in the rv Hamiltonian.

We proved that the considered models are realistic since they describe many important features of the rv energy spectrum correctly and the energy levels calculated for some classes of rv states are remarkably close to the observed ones.

Beyond the exact solutions we have also calculated analytically the approximate solutions for rv states lying in two regimes:

- (i) $J \leq 10$ and arbitrary K^\pm
- (ii) $J > 10$ and K is low or K is high.

Table 9. Exact solvable models of triatomic molecules. For six-dimensional models and exact kinetic energy operator solutions are exact for $(J, K^\pm) = (0, 0)$ and $(1, 1^-)$. For the remaining cases solutions are exact for $(J, K^\pm) = (0, 0)$, $(1, 0)$, $(1, 1^\pm)$, $(2, 1^\pm)$, $(2, 2^-)$ and $(3, 2^-)$.

Model	Potential function	Kinetic energy operator
Four-dimensional bending-rotation model	$V_b(\vartheta) = V_-/[2(1 - \cos \vartheta)] + V_+[2(1 + \cos \vartheta)] - V_0$	$r_k = r_e$; $\mathcal{D}_3^2(r_k) = 0$
Six-dimensional local model	$\begin{cases} V_L(r_1, r_2, \vartheta) = V(r_1) + V(r_2) + (r_1^{-2} + r_2^{-2}) V_b(\vartheta) \\ V(r_k) = D_e(1 - r_e/r_k)^2 \end{cases}$	Exact $\Lambda_-^2 = 0$
Six-dimensional collective model	$\begin{cases} V_C(R, \rho, \vartheta) = V_s(R) + 2R^{-2}[V_a(\rho) + \sin^{-2} \rho V_b(\vartheta)] \\ V_s(R) = D_e(1 - R_e/R)^2; V_a(\rho) = A(\sin^{-2} \rho - 1) \end{cases}$	Exact $\Lambda_-^2 = 0$

The solutions for high J allowed the analysis of the interesting physical effects occurring due to very strong centrifugal deformations of the rotating-vibrating molecule. Such deformations can change the hierarchy of the effective rotational constants which are sensitive to rotational excitations.

We have also found that the excited bending vibration can create a predissociation barrier similar to the barrier generated by rotations.

The obtained exact or approximate solutions due to their simple form and reasonable accuracy can be used as excellent basis functions in variational or perturbational calculations of RV wavefunctions and energy levels of triatomic molecules.

The RV Hamiltonian of a polyatomic molecule includes some typical operators such as \mathcal{D}_n^2 and Λ_m^2 (this fact will be proved in a separate paper). Thus, the presented wavefunctions can also be applied to polyatomic molecules.

References

- Abramowitz M and Stegun I A 1964 *Handbook of Mathematical Functions* (NBS) (Washington, DC: US Govt Printing Office)
- Antipov A B, Bykov A D, Zuev V E, Kapitanov V A, Lopasov V P, Makushkin Yu S, Tolmachev V I and Ulenikov O N 1982 *Opt. Spectrosc.* **53** 613
- Bunker P R 1983 *Ann. Rev. Chem. Phys.* **34** 59
- Bunker P R and Landsberg B M 1977 *J. Mol. Spectrosc.* **67** 374
- Child M S and Halonen L 1984 *Adv. Chem. Phys.* **57** 1
- Child M S and Lawton R T 1982 *Chem. Phys. Lett.* **87** 217
- Feynman R P 1939 *Phys. Rev.* **56** 340
- Flaud J M and Camy-Peyret 1976 *Mol. Phys.* **32** 499
- Fuess E 1926 *Ann. Phys., Paris* **80** 367
- Gausset L, Herzberg G, Lagerqvist A and Rosen B 1965 *Astrophys. J.* **142** 45
- Harter W G and Patterson C W 1984 *J. Chem. Phys.* **80** 4241
- Hellmann H 1937 *Einführung in die Quantenchemie* (Vienna: Deuticke)
- Herzberg G 1950 *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (New York: Van Nostrand Reinhold)
- Hougen J T, Bunker P R and Johns J W C 1970 *J. Mol. Spectrosc.* **34** 136
- Hoy A R, Mills L M and Strey G 1972 *Mol. Phys.* **24** 1265
- Johnson B R and Reinhardt W P 1986 *J. Chem. Phys.* **85** 4538
- Jungen Ch, Hallin K E J and Merer A J 1980 *Mol. Phys.* **40** 25
- Jungen Ch and Merer A J 1980 *Mol. Phys.* **40** 95

- Kraemer W P, Bunker P R and Yoshimine M 1984 *J. Mol. Spectrosc.* **107** 191
- Kratzer A 1920 *Z. Phys.* **3** 289
- Lew H 1976 *Can. J. Phys.* **54** 2028
- Makarewicz J 1987a *Mol. Phys.* **61** 547
- 1987b *Phys. Lett.* **121** 83
- 1988a *J. Phys B: At. Mol. Opt. Phys.* **21** 1803
- 1988b *J. Mol. Spectrosc.* **130** in press
- Rothman L S 1978 *Appl. Opt.* **17** 3517
- Simons G, Parr R G and Finlan J M 1973 *J. Chem. Phys.* **59** 3229
- Townes C H and Schawlow A L 1955 *Microwave Spectroscopy* (New York: McGraw-Hill)
- Wallace R 1975 *Chem. Phys.* **11** 189
- Wang S C 1929 *Phys. Rev.* **34** 243
- Wilson E B, Decius J C and Cross P C 1955 *Molecular Vibrations* (New York: McGraw-Hill)