Classification
 Physics Abstracts
 33.20E

Effect of bending vibration on rotation and centrifugal distortion parameters of XY_2 molecules. Application to the water molecule

V. I. Starikov, B. I. Makhanchev and V. G. Tyuterev

The Institute of Atmospheric Optics, USSR Academy of Sciences, Siberian Branch, Tomsk, 634055, USSR

(Reçu le 27 septembre 1983, accepté le 16 novembre 1983)

Résumé. — Ce travail présente le calcul du comportement anormal des paramètres de rotation et de distorsion centrifuge de la molécule H_2O à partir du potentiel Lorentz + quadratique d'ordre zéro. Des cas particuliers des formules générales de dépendance de ces paramètres en fonction du nombre quantique v_2 associé à la vibration de déformation angulaire sont discutés.

Abstract. — The calculation of the anomalous behaviour of rotation and centrifugal distortion parameters of H_2O molecule with a Lorentz + quadratic zero-order potential is presented. Particular cases of general giving the dependence of these parameters with respect to the quantum number v_2 associated with the bending vibration are discussed.

1. Introduction.

The anomalous behaviour of rotation and centrifugal distortion parameters as a function of the bending quantum number v_2 is one of the most interesting features in high-resolution vibration-rotation spectroscopy of XY_2 molecules. For the water molecule it was discussed first by Camy-Peyret and Flaud [1-4] on the basis of an analysis of fitted data. An explanation of this behaviour was suggested in references 5, 6. Here we present the result of calculations of rotational and quartic centrifugal distortion using a Lorentz + quadratic potential function for the H_2O molecule.

v_2 -dependent parameters in effective rotational Hamiltonian. — It is convenient to choose intramolecular coordinates according to Hougen, Bunker and Johns (HBJ) [8] : ρ is the bending variable, J_ρ its associate momentum, q_1 and q_3 are the normal coordinates associated with the small vibrations v_1 and v_3 . The Contact Transformations (CT) of the HBJ-Hamiltonian to an effective rotational Hamiltonian

$$H^{HBJ} \xrightarrow{CT} \mathcal{H}_{rot} = \sum_{xyz} \{ {}^{eff}B_\alpha^t J_\alpha^2 + \frac{1}{4} \tau_{\alpha\beta\gamma\eta}^t J_\alpha J_\beta J_\gamma J_\eta + \dots \} \quad (1)$$

which do not use any poorly convergent expansions in ρ are quite similar to those described in reference 7 for the ammonia molecule (see also [6]). Unlike the effective Hamiltonian used by

Hoy and Bunker [9] (reviewed by Sørensen [10]), the operator (1) is a purely rotational one. It can be reduced to Watson's form [11] since B_α^t and τ^t are constant but not functions of ρ as in [8-10].

On the contrary to the usual formulae for a semirigid molecule [12, 13] the leading contributions to the constants B and τ depend on the bending quantum number $t \equiv v_2$

$$^{\text{eff}} B_\alpha^t = \{ \langle \psi_t | B_\alpha(\rho) | \psi_t \rangle + \Delta B_\alpha^t \} + \sum_{k \neq 2} B_{\alpha,k}^t (v_k + \frac{1}{2}) \quad (2)$$

where the second-order contributions have the form

$$\begin{aligned} \Delta B_\alpha^t = & - \sum_{i \neq 2} \frac{\langle \psi_t | K_i(\rho) + B_i^{\rho\rho}(\rho) \mathfrak{J}_\rho^2 | \psi_t \rangle \langle \psi_t | B_i^{\alpha\alpha}(\rho) | \psi_t \rangle}{\omega_i} - \\ & - 2 \sum_{i,s} \frac{|\langle \psi_t | B_i^{\alpha\rho}(\rho) \mathfrak{J}_\rho | \psi_s \rangle|^2}{\omega_i^2 - (\varepsilon_s - \varepsilon_t)^2} \omega_i \quad (3) \\ B_{\alpha,k}^t = & \frac{3}{4} \left\langle \psi_t \left| \sum_{xyz\rho} [B_k^{\alpha\gamma}(\rho)]^2 B_\gamma^{-1}(\rho) \right| \psi_t \right\rangle + \sum_{i \neq 2} \left\{ 2 \frac{\langle \psi_t | C_{ik}^\alpha(\rho) B_\alpha(\rho) | \psi_t \rangle^2}{\omega_k} \frac{3 \omega_k^2 + \omega_i^2}{\omega_k^2 - \omega_i^2} - \right. \\ & - 3 \frac{\langle \psi_t | K_{kki}(\rho) | \psi_t \rangle \langle \psi_t | B_i^{\alpha\alpha}(\rho) | \psi_t \rangle}{\omega_i} \left. \right\} + 4 \sum_s \frac{|\langle \psi_t | B_k^{\alpha\rho}(\rho) \mathfrak{J}_\rho | \psi_s \rangle|^2 (\varepsilon_s - \varepsilon_t)}{\omega_k^2 - (\varepsilon_s - \varepsilon_t)^2} \\ & - 2 \sum_{s \neq t} \frac{\langle \psi_t | B_\alpha(\rho) | \psi_s \rangle \langle \psi_s | \omega_k(\rho) | \psi_t \rangle}{\varepsilon_s - \varepsilon_t}. \end{aligned}$$

Second-order formula for the centrifugal distortion constants reads [5, 6] :

$$\begin{aligned} \tau_{\alpha\beta\gamma\eta}^t = & - 2 \sum_{k \neq 2} \frac{\langle \psi_t | B_k^{\alpha\beta}(\rho) | \psi_s \rangle \langle \psi_s | B_k^{\gamma\eta}(\rho) | \psi_t \rangle}{\omega_k + (\varepsilon_s - \varepsilon_t)} - \\ & - 4 \sum_{s \neq t} \frac{\langle \psi_t | B_\alpha(\rho) | \psi_s \rangle \langle \psi_s | B_\gamma(\rho) | \psi_t \rangle}{\varepsilon_s - \varepsilon_t} \delta_{\alpha\beta} \delta_{\gamma\eta}. \quad (4) \end{aligned}$$

Here ε_ρ , ε_s and ψ_ρ , ψ_s are energies and wave-functions of the bending states ($0 \neq t$), ($0 \neq s$)

$$\{ T^{\text{bend}} + V_0(\rho) \} \psi_t(\rho) = \varepsilon_t \psi_t(\rho). \quad (5)$$

The kinetic energy operator T^{bend} associated with the nv_2 modes is that of reference 8.

2. Calculated parameters of the H₂O molecule.

In order to calculate the matrix elements appearing in equations 2-4 one has to know all the functions of $\rho_{\alpha\beta}$ involved. According to Hougen *et al.* [8] the functions $B_\alpha(\rho)$ and $B_k^{\alpha\beta}(\rho)$ are the following

$$B_\alpha(\rho) = h/8 \pi^2 c I_\alpha(\rho) \quad B_k^{\alpha\beta}(\rho) = - \frac{1}{2} (h/4 \pi^2 c)^{3/2} \omega_k^{-1/2}(\rho) \quad a_k^{\alpha\beta}(\rho)/I_\alpha(\rho) I_\beta(\rho)$$

where the $I_\alpha(\rho)$'s are given in reference 8. The inertia derivatives and Coriolis parameters take the forms

$$\begin{aligned} a_1^{\gamma\gamma}(\rho) &= a_0 \gamma^{-1} \cos^2(\rho/2) & a_1^{\alpha\alpha}(\rho) &= a_0 \gamma^{-1} & a_1^{\alpha\beta}(\rho) &= a_0 \gamma^{-1} \\ a_3^{\alpha\rho}(\rho) &= a_0 \beta^{-1} & a_3^{\gamma\gamma}(\rho) &= - \frac{1}{2} a_0 \beta^{-1} \sin \rho & C_{13}^\alpha &= \frac{1}{2} \kappa(\beta\gamma)^{-1} \sin \rho \end{aligned} \quad (6)$$

with the following notation

$$\begin{aligned} \gamma &= \{ 1 + \kappa \sin^2 (\rho/2) \}^{1/2} & \beta &= \{ 1 + \kappa \cos^2 (\rho/2) \}^{1/2} \\ \kappa &= 2 m_H/m_O & a_0 &= 2(2 m_H \Gamma_O^2)^{1/2}. \end{aligned} \quad (7)$$

The anharmonicity parameters $K_i(\rho)$, $K_{ijl}(\rho)$ and $\omega_i(\rho)$ are calculated according to the scheme of reference 9 where the only leading term in the expansion $\mathfrak{A}_i = \sum_k L_k^i(\rho) Q_k + \dots$ has been kept with the $L_k^i(\rho)$ functions given by

$$L_1^1(\rho) = L_1^3(\rho) = \gamma/\sqrt{2 m_H} \quad L_3^1(\rho) = -L_3^3(\rho) = \beta/\sqrt{2 m_H}. \quad (8)$$

The bending potential $V_0(\rho)$ in equation 5 has been taken to be a Lorentz + quadratic potential function :

$$V_0(\rho) = K\rho^2/2 + K_B/(C^2 + \rho^2). \quad (9)$$

Parameters in equation 9 are chosen in such a way that ε_i calculated from equation 5 restitutes the experimental vibrational energies. In figure 1a the dependence of $^{\text{eff}}B_z$ on the bending quantum number $t = v_2$ is presented for three values of barrier height. The higher the barrier (i.e. the more rigid the molecule), the smoother the behaviour of B^t . A similar regularity takes place for other parameters as well.

Fig. 1. — Calculated behaviour of B_z and A as a function of the bending quantum number v_2 for the water molecule. The lines —•— correspond to direct calculations using Eqs. 2-4 (the calculated behaviour of B_z , Δ_K , Δ_{JK} , Δ_J , δ_J presented in the figure and in the table was not fitted to the experimental one). A Lorentz + quadratic potential function $V_0(\rho)$ is used in the calculations with the following values of barrier height $H_I = 10\,155 \text{ cm}^{-1}$, $H_{II} = 10\,900 \text{ cm}^{-1}$, $H_{III} = 11\,600 \text{ cm}^{-1}$ used to reproduce the vibrational levels (0 1 0) (see references 8, 9, 5). Empty dots ○ and squares □ correspond to experimental values of references 1-4.

According to the well-known Nielsen's ordering scheme (based on expansions of the inertia tensor and of the potential function in all vibrational coordinates [12, 13]), the vibrational dependence of a spectroscopic parameter has to be two orders of magnitude less than the leading contribution. However the fitted parameters of H_2O [1-4] associated with the operators $\mathcal{J}_z^{2n}$ do not obey this scheme, they increase much more rapidly. Within the present approach the calculated v_2 behaviour of the spectroscopic parameters [5, 6] is in agreement with the experimental one [1-4]. In table I we present the parameters having the strongest v_2 dependence calculated with a Lorentz + quadratic potential. These are direct calculations performed without any adjustable parameter.

Table I. — *Calculated (*) and experimental values of the parameters $^{\text{eff}}B_z^t$ and Δ_K^t for H_2^{16}O .*

	cm^{-1}	(000)	(100)	(001)	(010)	(110)	(011)	(020)	(030)	(040)
fitted to experimental data [1-4]		27.88	27.12	26.65	31.13	30.17	29.52	35.56	42.05	52.65
$^{\text{eff}}B_z$ calculated Eq. 2		28.06	27.60	27.06	31.16	30.69	29.99	35.36	41.51	51.90
<hr/>										
		(000)	(010)	(020)	(030)					
fitted to experimental data [1-4]		3.24	5.76	11.3	26.0					
$\Delta_K \times 10^2$										
calculated Eq. 4		3.43	6.07	11.64	26.11					

(*) The potential (9) with the parameters $K = 11\,302\text{ cm}^{-1}$, $H = 11\,600\text{ cm}^{-1}$, $\gamma_e = \pi - \rho_e = 104.50^\circ$ is used; $\Gamma_0 = 0.957\text{ \AA}$ (see references 9, 5).

3. Particular cases of v_2 -dependent formulae for spectroscopic parameters.

In order to relate the present approach to more standard ones it is convenient to discuss the following particular cases of equation 4.

3.1 HARMONIC OSCILLATOR APPROXIMATION FOR THE BENDING VIBRATION IN THE ZERO-ORDER HAMILTONIAN (4). — One has :

$$\{ T^{\text{Bend}} + V_0(\rho) \} \sim \frac{1}{2} \omega_2 \left(-\frac{\partial^2}{\partial q_2^2} + q_2^2 \right), \quad \rho \sim \left(\frac{2 B_\rho}{\omega_2} \right)^{1/2} q_2 \quad (10)$$

$\varepsilon_t \sim \omega_2(t + \frac{1}{2})$ and $|\psi_t\rangle \sim |t\rangle$ where $|t\rangle$ are harmonic oscillator wave functions. In this case one has

$$\tau_{\alpha\beta\gamma\eta}^t = -2 \sum_{k \neq 2} \frac{\langle t | B_k^{\alpha\beta}(\rho) | s \rangle \langle s | B_k^{\gamma\eta}(\rho) | t \rangle}{\omega_k + \omega_2(s - t)} - 4 \sum_{s \neq t} \frac{\langle t | B_\alpha(\rho) | s \rangle \langle s | B_\gamma(\rho) | t \rangle}{\omega_2(s - t)} \delta_{\alpha\beta} \delta_{\gamma\eta}. \quad (11)$$

In fact in this particular case one expands the potential function $V = \frac{1}{2} \sum \omega_i q_i^2 + \dots$ in all

vibrational displacements (including q_2). This formula is closely connected with that of reference 14.

3.2 INERTIA TENSOR EXPANDED IN $\rho \sim \left(\frac{2 B_\rho}{\omega_2}\right)^{1/2} q_2$, ANHARMONIC ZERO-ORDER POTENTIAL FUNCTION $V_0(\rho)$. THE LEADING NON ZERO CONTRIBUTIONS IN EQUATION 4 ARE KEPT. — One obtains :

$$B_\alpha(\rho) = B_\alpha + B_2^{\alpha\alpha} q_2 + \dots, \quad B_k^{\alpha\beta}(\rho) = B_k^{\alpha\beta} + B_{k2}^{\alpha\beta} q_2 + \dots \quad (12)$$

$$\tau_{\alpha\beta\gamma\eta}^t = -2 \sum_{k \neq 2} \frac{B_k^{\alpha\beta} B_k^{\gamma\eta}}{\omega_k} - 4(B_2^{\alpha\alpha} B_2^{\gamma\gamma}) \sum_{s \neq t} \frac{|\langle \psi_t | q_2 | \psi_s \rangle|^2}{\varepsilon_s - \varepsilon_t} \delta_{\alpha\beta} \delta_{\gamma\eta}. \quad (13)$$

This formula is quite similar to that used by Creswell and Mills [15].

3.3 BOTH APPROXIMATIONS (10) AND (12) ARE USED IN EQUATION 4. — In this particular case one has the well-known Wilson-Howard formula for a semirigid molecule

$$\tau_{\alpha\beta\gamma\eta} = -2 \sum_k B_k^{\alpha\beta} B_k^{\gamma\eta} / \omega_k$$

which is independent on $t \equiv v_2$.

Acknowledgments.

We are pleased to thank G. Amat, P. R. Bunker, C. Camy-Peyret, J.-M. Flaud and Yu. S. Makushkin for very helpful discussions.

References

- [1] CAMY-PEYRET, C., FLAUD, J. M., *Mol. Phys.* **32** (1976) 523-537.
- [2] FLAUD, J. M., CAMY-PEYRET, C., *Mol. Phys.* **26** (1973) 811-823.
- [3] FLAUD, J. M., CAMY-PEYRET, C., *J. Mol. Spectrosc.* **51** (1974) 142-150.
CAMY-PEYRET, C., FLAUD, J. M., *Spectrochim. Acta* **29A** (1973) 1711-1715.
CAMY-PEYRET, C., FLAUD, J. M., *J. Mol. Spectrosc.* **59** (1976) 327-337.
- [4] CAMY-PEYRET, C., FLAUD, J. M., MAILLARD, J.-P., *J. Physique Lett.* **41** (1980) L-23-L-24.
- [5] STARIKOV, V. I., TYUTEREV, VI. G., On the theory of vib.-rot. spectra of nonrigid molecules (in Russian), Preprint N29, IAO, Tomsk, 1979, 66 pp.
STARIKOV, V. I., MAKHANCHEJEV, B. I., TYUTEREV, VI. G., in the book : *Spectroscopy of Atmospheric Gases*, Nauka, Novosibirsk, 1982, 34-54.
- [6] STARIKOV, V. I., TYUTEREV, VI. G., *J. Mol. Spectrosc.* **95** (1982) 288-296.
- [7] STARIKOV, V. I., TYUTEREV, VI. G., *Optika i Spectrosc.* **51** (1981) 268-277.
- [8] HOUGEN, J. T., BUNKER, P. K., JOHNS, J. W. C., *J. Mol. Spectrosc.* **34** (1970), 136-172.
- [9] HOY, A. R., BUNKER, P. R., *J. Mol. Spectrosc.* **52** (1974) 439-456.
- [10] SØRENSEN, G. O., *Topics in Current Chemistry* (Springer-Verlag, Berlin) 99-175.
- [11] WATSON, J. K. G., *J. Chem. Phys.*, **46** (1967) 1935-1949.
- [12] NIELSEN, H. H., *Rev. Mod. Phys.* **12** (1940) 175-185.
- [13] AMAT, G., NIELSEN, H. H., TARRAGO, G., *Rotation-Vibration of Polyatomic Molecules* (Dekker, New York) 1971.
- [14] MAKUSHKIN, YU. S., TYUTEREV, VI. G., *Phys. Lett.* **47A** (1974) 128-131.
- [15] CRESWELL, R. A., MILLS, I. M., *J. Mol. Spectrosc.* **52** (1974) 392-412.