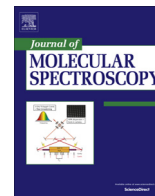




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# The bending potential energy function of HDO obtained from high-resolution data

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## ABSTRACT

Line position and line intensity analyses of the high-resolution spectrum of the HDO isotopic species of the water molecule are performed with an extended version of the Bending-Rotation approach up to the (010) state and  $J = 22$ . The line position analysis involves 3992 microwave, far infrared and infrared lines, and 421 experimental energy levels which were reproduced with a 1.1 unitless standard deviation. The data set considered in the line intensity analysis consists of 1405 infrared absorption lines and 4 Stark coefficients fitted with a 1.2 unitless standard deviation. The results of both analyses are compared with previous investigations and are used to build a spectroscopic database which is compared with other available databases and should be useful for interpreting measurements carried out with the Infrared Atmospheric Sounding Interferometer (IASI).

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## 1. Introduction

The HDO molecule is important in many areas and has been used, for instance, to study the atmosphere of terrestrial planets. Measurements of the ratio  $\delta D = [\text{HDO}]/[\text{H}_2\text{O}]$  were thus performed in the atmosphere of Venus [1] and Mars [2]. In the case of the earth atmosphere,  $\delta D$  is measured using satellite observations and contains information about many processes such as the transport experienced by the water mass [3,4] or global climatological behavior [5]. HDO is also interesting from the spectroscopic point of view as it displays an anomalous centrifugal distortion, evidenced a long time ago [6], similar to that of the normal species  $\text{H}_2\text{O}$  [7]. A model developed to treat the anomalous distortion in HDO should account for the fact that it lacks a two-fold axis of symmetry.

A new treatment aimed at the calculation of the rovibrational energy of the HDO molecule and accounting for anomalous centrifugal distortion effects has been developed. It is a modified version of the Bending-Rotation approach initially developed for the normal species [8–12] and also relies on an effective Hamiltonian in which the large amplitude bending  $\nu_2$  mode and the overall rotation of the molecule are treated simultaneously. Due to the lack of a two-fold axis of symmetry, this effective Hamiltonian contains terms arising from a non-diagonal component of the inertia

tensor and from the Coriolis coupling between the large amplitude bending  $\nu_2$  mode and the overall rotation of the molecule.

This new treatment has been used to perform a line position analysis of a large body of microwave [6,13,14], infrared [15–18], hot water vapor [19,20], and experimental levels [18] data involving the ground and (010) states up to  $J = 22$ . For these 4413 data, a unitless standard deviation of 1.1 was achieved. A line intensity analysis was also carried out and allowed us to reproduce the strength of 1405 transitions [16,18] and 4 Stark coefficients [21] with a unitless standard deviation of close to unity. The results of the line position analysis are compared with those of a previous investigation [22]. A Hitran-type spectroscopic database spanning the 0–2000  $\text{cm}^{-1}$  region is built and compared with HITRAN 2012 [23] and with the database built in Ref. [24] for planetological purposes.

This paper has four remaining sections. The extended version of the Bending-Rotation approach used for the rovibrational energy and line strength calculations is presented in Section 2. Section 3 deals with the line position and line strength analyses, and with the Hitran-type spectroscopic database. Section 4 is the discussion.

## 2. Theory

The Bending-Rotation approach [8–12] initially designed to account for anomalous centrifugal distortion effects in the normal species of water [7] is extended to molecules without a two-fold

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axis of symmetry as HDO. Like in Refs. [8–12], a bending-rotation Hamiltonian is built starting from the exact Hamiltonian of a triatomic molecule written using Radau's coordinates [25,26].

### 2.1. The bending-rotation Hamiltonian

The exact quantum mechanical Hamiltonian of a triatomic molecule is well known and can be found in Ref. [27] when the usual bond angle and bond lengths internal coordinates are used and in Ref. [28] when Radau coordinates are used. In this work, we will use the exact Hamiltonian in Eq. [1] of Ref. [29], also written with Radau coordinates, but where, instead of the Radau angular coordinate  $\theta$ , the bending coordinate  $t = \cos \theta$  is used. Just like in Ref. [8], terms involving the conjugated momenta  $P_{r_1}$  and  $P_{r_2}$  are ignored and the Radau stretching coordinates  $r_1$  and  $r_2$  are set to their equilibrium value  $r_{1e}$  and  $r_{2e}$ . This yields the following bending-rotation Hamiltonian:

$$H_{b-r} = B_e P_t (1 - t^2) P_t + V(t) + B_e \left[ \frac{J_x^2}{2(1-t)} + \frac{J_y^2}{4} + \frac{J_z^2}{2(1+t)} \right] + A_e \left[ J_y \{ \sqrt{1-t^2}, P_t \} - \frac{\{ J_x, J_z \}}{\sqrt{1-t^2}} \right], \quad (1)$$

where  $P_t$  is the momentum conjugated to  $t$ ;  $J_x$ ,  $J_y$ , and  $J_z$  are the components of the rotational angular momentum in the molecule-fixed axis system;  $\{, \}$  is the anticommutator;  $V(t)$  is the potential energy function; and  $B_e$  and  $A_e$  are two constants. (In Eq. (1), the term in  $A_e$  accounts for a typographical error in Eq. (1) of Ref. [29].)  $B_e$  and  $A_e$  can be expressed in terms of  $r_{1e}$ ,  $r_{2e}$  and the atom masses:

$$B_e = \frac{1}{2} \left( \frac{1}{m_1 r_{1e}^2} + \frac{1}{m_2 r_{2e}^2} \right), \quad A_e = \frac{1}{4} \left( \frac{1}{m_2 r_{2e}^2} - \frac{1}{m_1 r_{1e}^2} \right). \quad (2)$$

Assuming atoms 1 and 2 are the deuterium and hydrogen atoms, respectively, we obtain [30]  $r_{1e} = 0.9127$  and  $r_{2e} = 0.9467$  Å yielding  $B_e = 28.722$  and  $A_e = 4.310$  cm<sup>-1</sup>. As in the previous approaches [8–12], the potential energy function in Eq. (1) is approximated by a sixth order polynomial of  $t$ :

$$V(t) = \sum_{i=1}^6 V_i t^i, \quad (3)$$

where  $V_i$ , with  $1 \leq i \leq 6$ , are six constants.

Comparing the bending-rotation Hamiltonian obtained in Ref. [8] and the one obtained in this work shows that the lack of two-fold axis of symmetry leads to an extra term, the term in  $A_e$ . This term describes the Coriolis coupling between the overall rotation and the  $v_2$  mode and includes a non-diagonal contribution from the inertia tensor. This term gives rise to non-diagonal rotational matrix elements only.

### 2.2. Vibrational and rovibrational matrix elements

Like in Ref. [9], a bending Hamiltonian is extracted from the bending-rotation Hamiltonian in Eq. (1) retaining only those terms having diagonal rotational matrix elements between two usual symmetric top rotational functions  $|J, K\rangle$ , where the quantum number  $M$  is ignored for simplicity. The  $t$ -dependent bending Hamiltonian takes the following expression:

$$H_b = M_f P_t (1 - t^2) P_t + \sum_{i=1}^6 M_i t^i + \frac{1}{2} \left( \frac{M_+}{1+t} + \frac{M_-}{1-t} \right), \quad (4)$$

where  $M_f, M_+, M_-$ , and  $M_i$ , with  $1 \leq i \leq 6$ , are 9 constants given by:

$$\begin{aligned} M_f &= B_e, \\ M_+ &= B_e K^2, \\ M_- &= B_e [J(J+1) - K^2]/2, \\ M_i &= V_i, \quad \text{with } 1 \leq i \leq 6. \end{aligned} \quad (5)$$

Matrix elements of the bending Hamiltonian in Eq. (4) between two  $\theta_n^{\alpha\beta}(t)$  basis set bending functions, as defined in Eq. (4) of Ref. [9], take the following expression:

$$\langle \theta_n^{\alpha\beta} | H_b | \theta_{n'}^{\alpha\beta} \rangle = M_f v(v+1) \delta_{n,n'} + \sum_{i=1}^6 M_i \langle \theta_n^{\alpha\beta} | t^i | \theta_{n'}^{\alpha\beta} \rangle, \quad (6)$$

where in agreement with Refs. [8,9],  $\alpha$  and  $\beta$  are respectively  $\sqrt{M_-/M_f}$  and  $\sqrt{M_+/M_f}$ , and  $v = n + (\alpha + \beta)/2$ . Evaluation of the matrix elements of  $t^i$  in Eq. (6) can either be performed, using Table I of Ref. [9], when  $i \leq 4$ , or Eq. (A.1) of the present paper for any  $i$ -values. The matrix of the bending Hamiltonian  $H_b$  is setup using Eq. (6) for  $0 \leq n, n' \leq n_{\text{Max}}$ , where  $n_{\text{Max}}$  is a positive integer. Diagonalization yields bending energies and eigenfunctions which will respectively be written:

$$\begin{cases} E(v_2, M), \\ |v_2, M\rangle = \sum_{n=0}^{n_{\text{Max}}} C_n(v_2, M) | \theta_n^{\alpha\beta} \rangle, \end{cases} \quad (7)$$

where  $v_2$  is the vibrational quantum number for the bending  $v_2$  mode,  $M$  is a shorthand notation for the 9 constants defined in Eq. (5), and  $C_n(v_2, M)$  are real expansion coefficients.

Rovibrational matrix elements of the bending-rotation Hamiltonian are evaluated using the basis set rovibrational wavefunctions in Eq. (11) of Ref. [9]. We are led to evaluate the matrix element:

$$\langle \Psi_{v_2, J, K, \gamma} | H_{b-r} | \Psi_{v_2', J, K', \gamma'} \rangle, \quad (8)$$

which is nonvanishing if  $\Delta K = |K - K'| \leq 2$  and  $\gamma' = \gamma(-1)^{\Delta K}$ . When  $\Delta K = 0$  or 2, this matrix element can be retrieved from Eqs. (14) and (15) of Ref. [9] replacing  $H_0, H_+$  and  $H_-$  by  $B_e J_y^2/4, B_e J_z^2$ , and  $B_e J_x^2$ , respectively. These equations lead to rotational matrix elements that can be found in Refs. [31,32] and to the two bending matrix elements:

$$\langle v_2, M | Op | v_2', M' \rangle, \quad (9)$$

where  $Op$  is either 1 or  $1/(1-t)$ . These matrix elements should be computed using Eq. (16) of Ref. [9] where  $\langle \theta_n^{\alpha\beta} | Op | \theta_{n'}^{\alpha'\beta'} \rangle$  the matrix element on the right hand side of this equation can either be calculated using Eq. (17) of this reference or Eq. (A.1) of the present paper. When  $\Delta K = 1$ , the matrix element in Eq. (8) reduces to:

$$\begin{aligned} \langle \Psi_{v_2, J, K, \gamma} | H_{b-r} | \Psi_{v_2', J, K', \gamma'} \rangle &= \langle J, K, \gamma | H_y | J, K', \gamma' \rangle \\ &\quad \times \langle v_2, M | \{ \sqrt{1-t^2}, P_t \} | v_2', M' \rangle \\ &\quad + \langle J, K, \gamma | H_{xz} | J, K', \gamma' \rangle \\ &\quad \times \left\langle v_2, M \left| \frac{1}{\sqrt{1-t^2}} \right| v_2', M' \right\rangle, \end{aligned} \quad (10)$$

where

$$H_y = A_e J_y \quad \text{and} \quad H_{xz} = -A_e \{ J_x, J_z \}. \quad (11)$$

The rotational matrix elements of  $H_y$  and  $H_{xz}$  in Eq. (10) can be found in Refs. [31,32]. The bending matrix elements of  $\{ \sqrt{1-t^2}, P_t \}$  or  $1/\sqrt{1-t^2}$  can be computed using Eqs. (30) and (31) of Ref. [29] or Eqs. (A.1) and (A.4) of the present paper.

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