

# HDO absorption spectrum above $11\,500\text{ cm}^{-1}$ : Assignment and dynamics

B.A. Voronin <sup>a,b</sup>, O.V. Naumenko <sup>a</sup>, M. Carleer <sup>c</sup>, P.-F. Coheur <sup>c</sup>, S. Fally <sup>c</sup>, A. Jenouvrier <sup>d</sup>,  
R.N. Tolchenov <sup>b</sup>, A.C. Vandaele <sup>e</sup>, J. Tennyson <sup>b,\*</sup>

<sup>a</sup> Institute of Atmospheric Optics, SB, Russian Academy of Sciences, Tomsk, Russia

<sup>b</sup> Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

<sup>c</sup> Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, Brussels, Belgium

<sup>d</sup> Groupe de Spectrométrie Moléculaire et Atmosphérique, Reims, France

<sup>e</sup> Institut d'Aéronomie Spatiale de Belgique, Brussels, Belgium

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## Abstract

Assignment of an HDO line list extracted from a recently measured H<sub>2</sub>O/HDO/D<sub>2</sub>O Fourier transform absorption spectrum recorded in the  $11\,600\text{--}23\,000\text{ cm}^{-1}$  region by Bach et al. (M. Bach, S. Fally, P.-F. Coheur, M. Carleer, A. Jenouvrier, A.C. Vandaele, J. Mol. Spectrosc. 232 (2005) 341–350.) is presented. More than 94% of the 3256 lines are given quantum number assignments and ascribed to line absorption by HDO; most of the remaining lines are actually due to D<sub>2</sub>O. High accuracy variational predictions of line positions and intensities are used for the spectral assignment process. Assignments to the  $\nu_1 + 5\nu_3$ ,  $2\nu_2 + 5\nu_3$ ,  $\nu_1 + \nu_2 + 3\nu_3$  and  $\nu_1 + 6\nu_3$  bands are presented for the first time. Comparisons are made with published ICLAS spectra covering the same spectral region and suggestions made for its recalibration. The results are used to illustrate the dynamical behaviour of highly excited vibrational states of HDO and to discuss previous vibrational assignments to high lying rotation–vibration states of this system.

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## 1. Introduction

Numerous studies have been performed on the HD<sup>16</sup>O high resolution vibration–rotation spectrum in the near infrared and visible spectral regions [1–11]. These provide detailed information on the energy level structure of HD<sup>16</sup>O. Among these studies are a series of the intra cavity laser absorption spectroscopy (ICLAS) measurements [2–6,8] in the spectral regions dominated by the  $4\nu_3$  band at  $13853.628\text{ cm}^{-1}$ ,  $\nu_2 + 4\nu_3$  at  $15166.104\text{ cm}^{-1}$ ,  $\nu_2 + 3\nu_3$  at  $11969.753\text{ cm}^{-1}$ ,  $5\nu_3$  at  $16920.020\text{ cm}^{-1}$ ,  $2\nu_2 + 4\nu_3$  at  $16456.190\text{ cm}^{-1}$ ,  $\nu_2 + 5\nu_3$  at  $18208.446\text{ cm}^{-1}$ , and  $2\nu_2 + 3\nu_3$  band at  $13278.350\text{ cm}^{-1}$ . The  $5\nu_1$  band at  $12767.141\text{ cm}^{-1}$

was investigated using ICLAS with a Fourier transform spectroscopy (FTS) detection scheme [9,10], while the  $6\nu_3$  and  $7\nu_3$  bands at  $19836.882$  and  $22625.528\text{ cm}^{-1}$ , respectively, were studied for the first time by Jenouvrier et al. [7]. Finally, 11 energy levels with  $J \leq 3$  belonging to the most excited vibrational state studied to date, with vibrational energy of  $25140.85\text{ cm}^{-1}$ , were recently characterized by Theulé et al. [13] using two photon spectroscopy.

Prior to the study of Bach et al. [12] all HDO line intensities above  $11\,600\text{ cm}^{-1}$  were approximate values derived from peak absorptions and scaled using *ab initio* calculated values due to Partridge and Schwenke [14,15]. Accurate HD<sup>16</sup>O line intensities are known from Toth's measurements only in the spectral range below  $7700\text{ cm}^{-1}$  [16]. Thus the well known spectroscopic database HITRAN(2004) [17] includes HD<sup>16</sup>O absorption lines only

\* Corresponding author. Fax: +44 20 7679 7145.

E-mail address: [j.tennyson@ucl.ac.uk](mailto:j.tennyson@ucl.ac.uk) (J. Tennyson).

up to  $7500\text{ cm}^{-1}$ . In this connection the recently reported  $\text{HD}^{16}\text{O}$  line parameters measurements [12] based on the long pathlength FTS recordings over a wide spectral range from  $11\,500$  to  $23\,000\text{ cm}^{-1}$  are of importance for many applications including atmospheric studies where the simultaneous measurement of HDO and  $\text{H}_2^{16}\text{O}$  columns are used to provide valuable information on water circulation [18].

The experimental determination of the spectral line parameters provides an important starting point for theoretical models of molecular absorption and emission at different wavelengths, pressures and temperatures. A first necessary step in the theoretical treatment of an experimental line list is quantum assignment of the absorption lines. This study is devoted to identification of the experimental  $\text{HD}^{16}\text{O}$  absorption lines recorded by Bach et al. [12] using high quality variational calculations based on the work of Partridge and Schwenke [14,15] combined with spectral simulation within an effective Hamiltonian approach. A comparison of the results obtained with the available literature data is given.

Some interesting features of the  $\text{HD}^{16}\text{O}$  intra-molecular dynamics are revealed by the process of spectral assignment. These and the relationship of this work to previous studies of  $\text{HD}^{16}\text{O}$  visible spectra are discussed.

The intra-molecular dynamics of the HDO molecule differs significantly from that of the parent  $\text{H}_2^{16}\text{O}$  species due to the decrease in symmetry from  $C_{2v}$  to  $C_s$  and a considerable change in harmonic frequencies. In particular, the  $\omega_3$  frequency ( $3887\text{ cm}^{-1}$ ) corresponding to OH stretch is much larger than the  $\omega_1$  for the OD stretch ( $2823\text{ cm}^{-1}$ ) and  $\omega_2$  for the bending vibration ( $1444\text{ cm}^{-1}$ ). This results in a series of the well isolated ( $00v_3$ ) vibrational states. However, the close coincidence between the  $\omega_1$  and  $2\omega_2$  harmonic frequencies combined with abnormal centrifugal distortion effects gives rise to strong high-order resonance interactions in HDO, examined both in the previous ICLAS studies and the present work. The direct observation of states with the very highly excited bending modes such as (0120) and (1110) at  $14565.47$  and  $16049.01\text{ cm}^{-1}$ , respectively, were reported by Naumenko and co-workers [3,6]. Here we seek confirmation that such states are reachable from the ground vibrational state, and are just not an artifact of a vibrational labelling problem.

Due to large detuning (more than  $1000\text{ cm}^{-1}$ ) between  $\omega_3$  and  $\omega_1$  harmonic frequencies of  $\text{HD}^{16}\text{O}$ , the highly excited OH stretching states represent localized states which are of particular interest for the study of bond selective chemistry [13,19]. These investigations often involve using simple models such as the Morse oscillator to reproduce the O–H bond stretching assuming that all the excitation energy is localized on the O–H bond. The use of such approaches relies heavily on correct vibrational labelling of the states under study. Here we check and re-analyze the vibrational assignment of Theulé et al. [13].

The next section gives a summary of the experiments reported by Bach et al. [12]. Section three presents our line

assignments and the resulting energy levels we determine. Section four gives an extensive comparison with previous experimental studies. Section five discusses the intra-molecular dynamics of HDO in light of our results. Finally our conclusions are summarized in section six.

## 2. Experimental details

$\text{HD}^{16}\text{O}$  spectra were recorded using a high-resolution Fourier transform spectrometer (Bruker IFS120M) at  $15\text{ cm}$  optical path difference ( $0.06\text{ cm}^{-1}$  resolution) with a path length of  $600\text{ m}$ . The gas sample was composed of a  $\text{HD}^{16}\text{O}/\text{D}_2^{16}\text{O}/\text{H}_2^{16}\text{O}$  mixture at a total pressure of  $13\text{ hPa}$ . The  $\text{HD}^{16}\text{O}$  pressure was calculated to be  $6.3\text{ hPa}$ , see Table 1 in Bach et al. [12] for more details. Measurements were performed from the near infrared to the visible region at  $291\text{ K}$ . The experimental set-up is described in more detail elsewhere ([20] and references therein).

$\text{HD}^{16}\text{O}$  lines were isolated in the spectra by removing the  $\text{H}_2^{16}\text{O}$  lines contribution, as well as the atmospheric  $\text{H}_2^{16}\text{O}$  and  $^{16}\text{O}_2$  contributions (due to the absorption within the external path between the light source and the spectrometer), as explained in [12]. Briefly, the  $\text{H}_2^{16}\text{O}$  absorption lines were subtracted using a simulated spectrum generated from the  $\text{H}_2^{16}\text{O}$  Brussels–Reims (BR) database [20–22] and available at <http://www.ulb.ac.be/cpm>. The atmospheric  $\text{O}_2$  component was similarly removed using line parameters from the HITRAN database [17]. The  $\text{D}_2^{16}\text{O}$  lines belonging to the  $4v_1 + v_3$  band were identified in the region  $12\,000$ – $13\,000\text{ cm}^{-1}$  but not removed due to the lack of line parameters. As discussed below some other  $\text{D}_2\text{O}$  lines were also erroneously included in the HDO line list.

Table 1  
Fitted spectroscopic constants, in  $\text{cm}^{-1}$ , and dipole transition moment parameters, for the (006) and (007) vibrational states of HDO

	(006)	(007)
$E_v$	19836.88860(450)	22625.58085(930)
$A$	17.622094(680)	16.82551(220)
$B$	9.028960(380)	9.00563(130)
$C$	5.937600(310)	5.86906(110)
$A_k \times 10^3$	8.3835(280)	8.532(100)
$A_{jk} \times 10^3$	−0.6032(170)	−2.0332(931)
$A_j \times 10^4$	4.0555(190)	5.3465(970)
$\delta_k \times 10^3$	1.39783(420)	1.569(210)
$\delta_j \times 10^4$	1.4926(140)	2.3818(970)
$H_k \times 10^5$	2.0579	2.0579
$H_{jk} \times 10^7$	4.684	4.684
$h_k \times 10^5$	3.924(180)	
$N_{\text{lev}}$	69	40
$N_{\text{par}}$	10	9
RMS	0.013	0.020
$\mu_{1a}$ (D)	0.0042	0.0015
$\mu_{1b}$ (D)	0.0010	0.0004

$1\sigma$  confidence intervals are given in parenthesis. Parameters without confidence intervals were fixed to those of the (005) state [5].

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