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ICLAS of HDO between 13,020 and 14,115 cm^{-1}

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The high resolution absorption spectrum of monodeuterated water, HDO, has been recorded by Intracavity Laser Absorption Spectroscopy (ICLAS) in the 13,020–14,115 cm^{-1} region dominated by the $4\nu_3$ band. The achieved noise equivalent absorption (α_{min}~10^{-9} cm^{-1}) allowed detecting transitions with line strengths as small as 2×10^{-27} cm/molecule which is about 10 times lower than the smallest line intensities previously detected in the region.

The rovibrational assignment of the spectrum was based on the results of the variational calculations of Schwenke and Partridge (SP) as well as recent calculations using a new potential energy surface performed by Voronin, Tolchenov and Tennyson (VTT). 2157 transitions involving 21 upper vibrational states were assigned to $HD^{16}O$ while only four bands were previously reported in the region. A set of 157 new energy levels could be derived. It includes rotational levels of several highly excited bending states, in particular the (0 11 0) pure bending state. For some states like the (1 0 3) and (0 2 3) Fermi dyad, effective Hamiltonian modelling was needed to establish the vibrational assignments of some rotational levels. VTT calculations were found to significantly improve the SP results, the *rms* deviation of the calculated and observed energies being decreased from 0.23 to 0.06 cm^{-1}.

Finally, 79 transitions of the $4\nu_3$ band of the $HD^{18}O$ isotopologue were assigned, leading to the derivation of 48 levels, which are the most excited energy levels reported so far for this isotopologue.

1. Introduction

The stronger absorption lines of $H_2{}^{16}O$ and its isotopologues are well known from the microwave to the visible regions. However, weak transitions involving highly excited energy levels are still not properly accounted both experimentally and theoretically. This contribution is aimed at recording and assigning the weak $HD^{16}O$ transitions between 13,020 and 14,115 cm^{-1} which includes the strong $\Delta V_{OH}=4$ stretching overtone centred at 13853.6 cm^{-1}. The strongest HDO lines of the region have intensities in the order of 10^{-23} cm/molecule which makes difficult the detection of transitions with intensity at the 10^{-26} cm/molecule level. A further difficulty is due to the inevitable superposition with strong absorption lines of similar intensity due to the main isotopologue and with weaker lines of the D_2O species.

Ten years ago, we obtained the first HDO spectra in the region by Intracavity Laser Absorption Spectroscopy (ICLAS) using dye lasers as ICLAS spectrometers [1,2]. More recently, the wide 11,500–23,000 cm^{-1} region was studied by Fourier Transform Spectroscopy (FTS) associated with a 600 m absorption pathlength [3]. A similar sensitivity (about 2×10^{-26} cm/molecule for pure HDO)

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was achieved in the two studies. The present work is intended to achieve a higher sensitivity by using a titanium sapphire laser instead of dye lasers for ICLAS. It will allow (i) completing the previous measurements by new observations of weak transitions beyond the FTS sensitivity (ii) replacing our first ICLAS line lists [1,2] by a more complete dataset where the calibration problem (in the order of 0.01 cm^{-1}) evidenced [3] for the 13,100–13,500 cm^{-1} region [2] will be corrected. The increased sensitivity of the new recordings is demonstrated in Fig. 1, where the new ICLAS observations are superimposed to the FTS [3] spectrum.

The rovibrational assignment was performed on the basis of Schwenke and Partridge (SP) predictions [4,5] and recent variational calculations by Voronin, Tolchenov and Tennyson (VTT) [6] using a new HD^{16}O potential energy surface (PES) [7]. SP line lists of HD^{16}O and HD^{18}O can be downloaded from the IAO database [9].

Note that the same ICLAS:Ti–Sa set up was recently used to investigate the $H_2{}^{16}O$ [10] and D_2O [11,12] spectra in the same region. The obtained line lists will be used in the assignment process to discriminate the D_2O and $H_2{}^{16}O$ transitions superimposed with the HDO lines. Finally, it is worth mentioning that the analysis of the ICLAS spectrum of HDO has been reported recently [13] in the nearby 12,145–13,160 cm^{-1} region corresponding to much weaker HDO absorption lines.

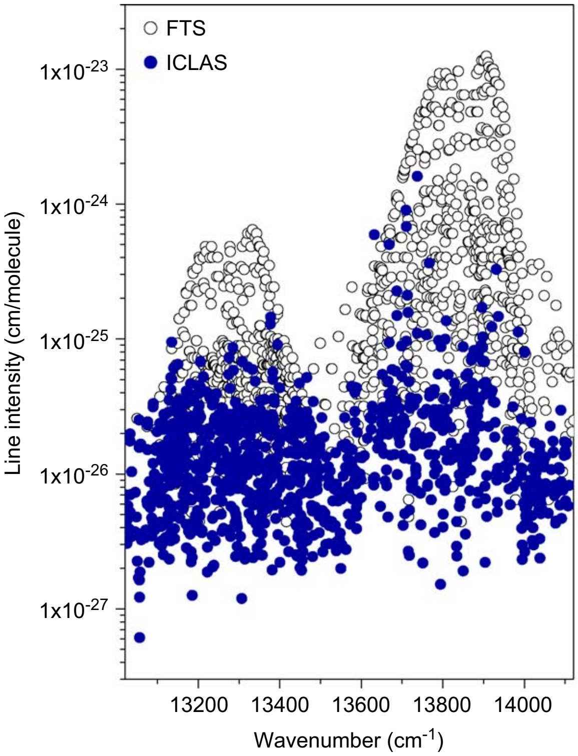

Fig. 1. Overview comparison of the HDO spectrum in the 13,020–14,115 cm^{-1} region. The transitions newly measured by ICLAS are superimposed to the previous FTS measurements of Ref. [3].

2. Experimental details

The spectra were recorded with the ICLAS spectrometer based on a Ti:Sapphire laser described in Refs. [10,14,15]. The occupation ratio of the laser cavity by the 65-cm-long absorption cell was 42%. The spectra were recorded with a generation time of 190 μs corresponding to an equivalent absorption pathlength of about 24 km. The intracavity sample cell was filled at a typical pressure of 18.4 hPa. Deuterated water was obtained by mixing liquid H_2O and D_2O. Two D_2O:H_2O mixing ratios were used for the recordings: below 13,550 cm^{-1}, D_2O and H_2O were mixed in equal quantities leading to a 1:2:1 proportion for H_2O:HDO:D_2O. Above 13,550 cm^{-1}, a higher deuterium enrichment was used in order to decrease the absorption of the strong $\Delta V_{OH} = 4$ stretching overtone of $H_2{}^{16}O$ which may obscure many HDO lines. The D_2O absorption being very weak [11,12], we used a 5:1 mixing ratio for D_2O and H_2O in the liquid phase. It led to a factor of 10 for the HDO:H_2O relative concentration which helped to detect very weak HDO lines. The contribution of the intracavity air (oxygen A band below 13,160 cm^{-1} and water vapor) was minimized by flowing continuously dry nitrogen in the box containing the Ti:Sa laser.

The ICLAS spectrum was obtained by successive recordings of 12 cm^{-1} wide spectral sections with the help of a 3754 diode silicon array. The 13,020–14,115 cm^{-1} region was covered by a total of 124 spectral snapshots overlapping by about 3 cm^{-1} on each side. Each of these individual spectra was calibrated independently using reference line positions. As far as possible we adopted the FTS line positions reported in Ref. [3] as reference lines. In some spectral sections, this line list was too sparse and we used the $H_2{}^{16}O$ line positions of Ref. [16]. Finally, in the lower energy region below 13,160 cm^{-1}, $H_2{}^{16}O$ and HDO lines are very weak and we took advantage of the transitions of the oxygen A band (due to residual oxygen inside the Ti:Sa cavity) to calibrate the spectra. The lack of precise reference lines may have led to errors up to 0.010 cm^{-1} in some very limited cases but we estimate that the accuracy of the wavenumber calibration is in the order of 0.005 cm^{-1} as it will be confirmed below by the uncertainty obtained for the energy levels retrieved from several transitions.

The line positions and relative line intensities were determined by using an interactive least squares multilines fitting program assuming a Voigt profile for each line. The position and integrated absorbance of each line were derived from the multiline fitting procedure. The analysis was made difficult by the numerous strong absorption lines saturated in our spectra. As our measurements were mostly devoted to weak lines, some strong lines with distorted intensity and centre were excluded from the line lists below 13,750 cm^{-1}. Above this value, some transitions have intensities in the order of 10^{-23} cm/molecule i.e. more than 1000 times larger than our detectivity threshold. In such conditions, we preferred to limit the line profile fittings to spectral intervals showing newly observed HDO transitions.

The difficulty to estimate accurately the HDO partial pressure in the ICLAS cell added to the uncertainty on the