

Emission spectrum of hot HDO below 4000 cm⁻¹

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Abstract

Fourier transform emission spectra were recorded using a mixture of H₂O and D₂O at a temperature of 1500°C. The spectrum was recorded the wavenumber range 1800 – 3932 cm⁻¹. This spectrum is analyzed together with a previously reported one spanning the 380 – 2190 cm⁻¹ range (Parekunnel et al., *J. Mol. Spectrosc.* **210**, 28 (2001)). This analysis leads to 4409 newly assigned HDO emission lines. This work particularly extends data on the (200) and (120) states of HDO for which newly determined energy levels are presented.

Key words: water vapor; infrared spectrum; emission; line assignments; hot bands

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1 Introduction

There have been a number of recent significant advances in the study of the spectrum of water [1]. In particular the use of laboratory emission spectroscopy [2] has yielded a large number of new lines which, when combined with absorption spectra recorded in sunspots, has yielded a wealth of new data on hot H_2^{16}O [3–8].

Significantly less attention has been paid to the spectrum of HDO, particularly that of hot HDO. However HDO is an important species in its own right for reasons as diverse as the study of D/H ratios in various locations in the Universe to tests of the failure of the Born-Oppenheimer approximation, where the symmetry breaking effect of single deuteration is expected to be strongest [9]. Recently, in a paper henceforth referred to as I [10], we reported the observation and assignment of the first emission spectrum of hot ($T = 1500^\circ\text{C}$) HDO. This spectrum spanned the $380 - 2190 \text{ cm}^{-1}$ region. In the present work we report on a new HDO emission in the $1800 - 3932 \text{ cm}^{-1}$ region. Since this spectrum overlaps our previously reported one and since the assignment of new transitions leads to further new assignments, we report here a combined analysis of both spectra which therefore cover the range 380 to 3932 cm^{-1} . Most of this region has been the subject of a recent detailed study at room temperature by Toth [11].

2 Experimental details

The hot HDO spectrum was recorded in November 1997 at the University of Waterloo with a Bruker IFS 120 HR Fourier transform spectrometer. The spectrometer was operated with a KBr beamsplitter and an InSb detector. A longwave pass filter at 4000 cm^{-1} was used. 40 scans were co-added at a resolution of 0.01 cm^{-1} . A CaF_2 window was used on the emission port of the spectrometer. The water vapor was heated in the center of a 1.2 m long, 5 cm diameter alumina tube sealed with cooled CaF_2 windows. The tube was placed inside a furnace and heated to 1500°C . A slow flow of water vapor was maintained through the cell at a pressure of 2.5 Torr. An equimolar mixture of H_2O and D_2O was used to provide the vapor. The thermal emission from the cell was focused into the emission port of the spectrometer with a parabolic mirror.

The lines were measured with the WSpectra program of M. Carleer and have an estimated accuracy of $\pm 0.001 \text{ cm}^{-1}$ for strong unblended lines. The spectrum was very dense with H_2O , HDO, and D_2O lines present. A sample portion of the spectrum, with the line assignments discussed below, is presented

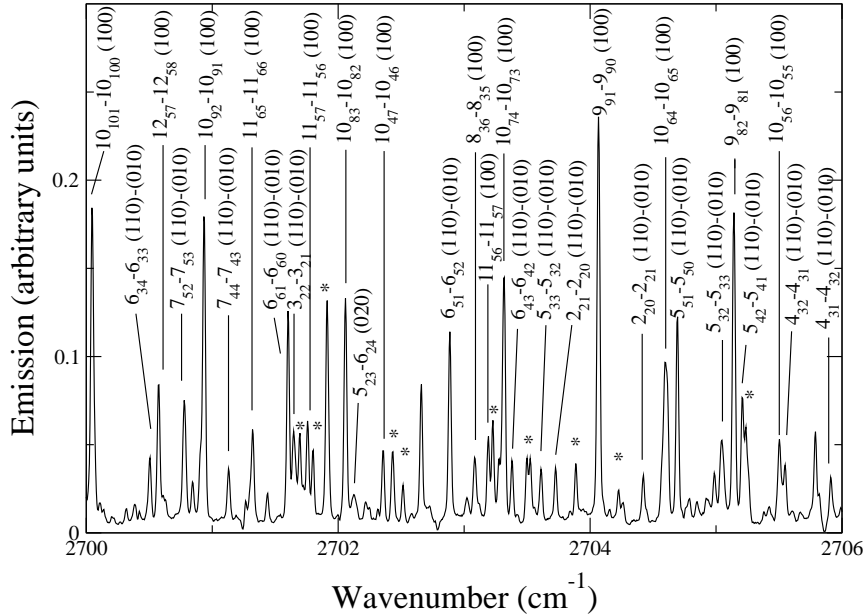


Fig. 1. Sample portion of the hot HDO emission spectrum. Line assignments are for HDO transitions. Starred lines are due to D₂O.

in Figure 1.

Lines were found throughout the 1800 – 3932 cm⁻¹ region. Because a substantial fraction of the lines in this spectrum are actually due to H₂O, it was calibrated against a previously reported hot water scale in this region [6]. A similar spectrum, not analyzed here, was recorded for fairly pure D₂O which allowed us to identify lines associated with emission of D₂O.

3 Line assignments

Our previous study, I, of hot HDO covered the 380 – 2190 cm⁻¹ range. Because both the high end of this range overlaps the present spectrum and the stretching fundamental bands straddle the spectrum, we chose to analyze both together. The 380 – 2190 cm⁻¹ region spectrum analyzed previous was merged with the present spectrum in the 1800 – 2190 cm⁻¹ region to give a total of 23 200 lines. The file containing these lines is given in the supplementary data.

The first step in our analysis is to identify those lines belonging to HDO emission. In our experimental line list, 3515 lines could be identified as belong to H₂O and a further 5357 lines as belonging to D₂O by comparison with

published hot emission spectra of H₂O and unpublished D₂O spectra. Lines were identified as H₂O or D₂O by matching both frequency and intensity. This is because the line density of the spectra is such that inevitably some HDO lines coincide with lines from the other isotopomers. Particularly for the case of D₂O spectrum this comparison is not always clear cut since the spectrum of D₂O actually contains HDO lines and there are also many blended lines. In our analysis we emphasized the HDO transitions; a significant number of the lines we analyze as HDO are actually blended with lines of H₂O or D₂O.

A similar, separate analysis was conducted for the 2190 – 3932 cm⁻¹ region for which spectra of hot HDO have not been reported previously. This region contained a total of 8456 lines; we identified 3069 as belonging to hot D₂O emissions and 998 lines as belonging to hot H₂O emissions.

The next step in our analysis was to try and make ‘trivial’ assignments using known HDO rotation-vibration energy levels. For this purpose the energy levels for the various HDO vibrational states of interest here with low J and K_a values reported by Toth [11–14] and others [15–17] were augmented by higher levels for these states and levels for (040) reported by us in I. 6430 HDO transitions were assigned in the 380 – 2190 cm⁻¹ region in I; a further 716 lines in the augmented spectrum in this region were given trivial assignments in this region as part of this work. 1815 lines in the not previously analyzed 2190 – 3932 cm⁻¹ region were assigned trivially.

To identify transitions involving previously unobserved energy levels in the system it was necessary to use variational predictions to aid the assignment process. There is no linelist available to us for hot HDO, but Partridge and Schwenke [18] have computed a room temperature linelist with states extending to energies about 8000 cm⁻¹ above the ground state. This linelist was transformed to a temperature of 1800 K using Boltzmann statistics. This list was augmented with energy levels for HDO states with higher rotational excitation provided by Schwenke. These levels could be used to help follow obvious sequences of transitions but the lack of intensities made them unsuitable for assigning completely new bands.

Having eliminated trivial assignments and other isotopomers from our list of transitions, the unassigned lines were analyzed using a computer program. Candidate transitions were identified using the variational linelist and then confirmed, or discarded, by the presence or lack of the appropriate combination difference transitions. In this way we were able to identify numerous new transitions involving known vibrational states. Our new spectra are particularly rich in transitions involving one change in the stretching quantum numbers.

In the 380 – 2190 cm⁻¹ region we have assigned a further 626 transitions

involving states for which at least one energy level was not previously known. This means that in this region a total of 1342 newly assigned HDO transitions can be added to the 6430 transitions assigned in I. In the higher 2190 – 3932 cm^{-1} region, 1252 transitions were assigned to states with new energy levels.

The file containing the experimental transitions given in the supplementary data has lines identified as belonging to H_2O or D_2O , where appropriate, and gives our line assignments for HDO transitions. In the newly analyzed region, 2190 – 3932 cm^{-1} , over 85% of the transitions have been marked in this fashion. Only about 65% of the transitions have been so marked in the lower wavenumber region. This is because there are significant portions of this region for which data on the emission of hot D_2O are not available.

Table 1 gives a breakdown of the 2439 newly assigned energy levels for HDO. Trivial assignments were also made to other states not listed in the table, such (021), (101), (002) and (210), using known data [14,17]. The tables distinguish between levels to which more than one transition has been assigned, and which are therefore confirmed by combination differences, and those for which only a single transition has been observed. The latter assignments must be considered less secure. We note that the presence of the many H_2O and D_2O lines in the spectrum makes it difficult to confirm assignments using combination differences. As noted in the table our analysis suggests that for 42 levels the data given in previously published tabulations is not correct.

Analysis of our new infrared emission spectrum has allowed us to determine many new energy levels for states involving stretching excitations, in particular (100), (001), (110), (011), (120) and (200). These new levels are tabulated in the electronic archive. This compilation augments that given in I which largely covered states with bending excitation.

4 Conclusions

Emission spectra recorded in a mixture of H_2O and D_2O have been analyzed together to give a list of 656 lines. Of these lines, 10839 have been assigned to transitions of HDO; the majority of the remaining lines have been identified as belonging to emissions of H_2O or D_2O by comparison with emission spectra of the species. The new assignments have allowed us to build up a significant dataset of HDO energy levels which are available both for further spectral analysis and to provide a rigorous test of theoretical models.

Table 1
 Summary of newly assigned HDO energy levels.

State	origin / cm^{-1}	a	b	c	total
(000)	0.00	119	348	9	467
(010)	1403.48	281	154	2	435
(020)	2782.01	253	72		325
(100)	2723.68	216	96	2	312
(001)	3707.47	186	46	19	232
(030)	4145.47	168	74	2	242
(110)	4099.96	178	36	2	214
(011)	5089.54	42	32	5	74
(040)	5420.04	48	8		56
(120)		13	11		24
(200)	5363.83	14	44	1	58

a New energy levels confirmed by combination differences.

b New energy levels not confirmed by combination differences.

c Energy levels which differ from previous compilations.

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References

- [1] P. F. Bernath, *Phys. Chem. Chem. Phys.* 4 (2002) 1501–1509.
- [2] P. F. Bernath, *Chem. Soc. Rev.* 25 (1996) 111–115.
- [3] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, L. Wallace, *Science* 277 (1997) 346–349.
- [4] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, L. Wallace, *Astrophys. J.* 489 (1997) L205–L208.
- [5] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, L. Wallace, *J. Molec. Spectrosc.* 186 (1997) 422–447.

- [6] N. F. Zobov, O. L. Polyansky, J. Tennyson, S. V. Shirin, R. Nassar, T. Hirao, T. Imajo, P. F. Bernath, L. Wallace, *Astrophys. J.* 530 (2000) 994–998.
- [7] K. Tereszchuk, P. F. Bernath, N. F. Zobov, S. V. Shirin, O. L. Polyansky, N. Libeskind, J. Tennyson, L. Wallace, *Astrophys. J.* 577 (2002) 496–500.
- [8] J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polyansky, P. F. Bernath, *J. Phys. Chem. Ref. Data* 30 (2001) 735–831.
- [9] N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, J. Tennyson, *Chem. Phys. Lett.* 260 (1996) 381–387.
- [10] T. Parekunnel, F. Bernath, N. F. Zobov, S. V. Shirin, O. L. Polyansky, J. Tennyson, *J. Molec. Spectrosc.* 101 (2001) 28–40.
- [11] R. A. Toth, *J. Molec. Spec.* 195 (1999) 73–97.
- [12] R. A. Toth, *J. Molec. Spec.* 162 (1993) 20–40.
- [13] R. A. Toth, J. W. Brault, *Appl. Optics* 22 (1983) 908–926.
- [14] R. A. Toth, *J. Molec. Spec.* 186 (1997) 66–89.
- [15] A. Perrin, C. Camy-Peyret, J.-M. Flaud, *Can. J. Phys.* 64 (1986) 736–742.
- [16] S.-M. Hu, O. N. Ulenikov, E. S. Bekhtereva, S.-G. He, X. Wang, H. Lin, Q.-S. Zhu, *J. Molec. Spec.* 203 (2000) 228–234.
- [17] O. N. Ulenikov, S.-M. Hu, E. S. Bekhtereva, G. A. Onopenko, X. Wang, S.-G. He, J.-J. Zheng, Q.-S. Zhu, *J. Molec. Spec.* 208 (2001) 224–235.
- [18] H. Partridge, D. W. Schwenke, *J. Chem. Phys.* 106 (1997) 4618–4639.