

Emission spectrum of hot HDO in the 380 – 2190 cm^{-1} region

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Fourier transform emission spectra were recorded using a mixture of H_2O and D_2O at a temperature of 1500°C . The spectra were recorded in three overlapping sections and cover the wavenumber range 380 – 2190 cm^{-1} . 22106 lines were measured of which 60 % are thought to belong to HDO. 6430 HDO transitions are assigned including the first transitions to the (040) vibrational state, with a term value of 5420.042 cm^{-1} . 1536 new energy levels of HDO belonging to the (000), (010), (020), (030) and (040) states are presented, significantly extending the degree of rotational excitation compared to previous studies.

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

1. INTRODUCTION

In recent years there has been great progress in the experimental and theoretical understanding of the energy level structure of water (1). On the experimental side, new overtone spectra of water have been recorded in the visible and near UV region (2-3). In the infrared, new spectra of hot water emission have now been measured (4-7) from 400 to 6000 cm^{-1} in the laboratory. Hot water vapor lines have also been seen in absorption in the spectra of sunspots (4, 6, 8) ("Water on the Sun"). On the theoretical side, the availability of high quality ab initio potential energy surfaces (9) and the direct variational calculation of vibration-rotation energy levels have revolutionized the analysis of water spectra (10).

Progress for the HDO isotopomer has been much less satisfactory. In particular, no spectra of hot HDO have been analyzed to date, and we report on such observations in this paper.

The HDO molecule is of interest for a number of reasons. Because H_2O is so abundant in our atmosphere, HDO can be detected readily in atmospheric absorption spectra using the sun as a source (11). Astrophysicists are also interested in HDO because nearly all of the deuterium now in the Universe was formed in the Big Bang (12). The D/H ratio is thus an important parameter with cosmological significance. The ratio of D/H can be determined for objects such as comets from the relative HDO to H_2O abundances (13).

In molecular physics, the HDO energy levels can be used to study the breakdown of the Born-Oppenheimer approximation. At the moment, this breakdown is the largest source of error in the calculation of water vibration-rotation energy levels from an ab initio potential energy surface. The potential surface can be corrected empirically (9-10), but recently Schwenke (14) has calculated ab initio a complete set of corrections for the breakdown of the Born-Oppenheimer approximation in water. The experimental energy levels of both HDO and H_2O are needed for comparison with theory. The HDO molecule is also a popular molecule for mode selective laser chemistry by dissociation (e.g., 15).

The infrared spectra of HDO were first measured by Benedict, Gailar and Plyler (16) in 1956, followed by work in France (e.g., 17). Since then there has been considerable additional work mainly by Toth and co-workers (18-23) on the room temperature infrared absorption spectra. Toth has recently published a list of the energy levels for the (000), (010), (100) and (020) vibrational states of HDO. Note that we adopt the traditional labeling convention of ν_1 for the OD stretching mode and for the ν_3 OH stretching mode, in spite of the Mulliken convention (24). Other infrared measurements include the detection of several transitions near 1 μm by Bykov et al. (25-26) and the 300 – 000 and 111 – 000 bands by Hu et al. (27).

The pure rotational lines of HDO were measured in the sub-millimeter wave region by Messer et al. (28) and by Baskakov et al. (29). To higher frequency, the pure rotational transitions

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in 20 – 350 cm^{-1} (30) and 110 – 500 cm^{-1} (31) regions were recorded by Fourier transform absorption spectroscopy.

The most highly-excited levels of HDO have been recorded by overtone spectroscopy in the visible and near UV region. Most notably, Campargue and co-workers (32-36) have recently used the ultrasensitive technique of intracavity laser absorption spectroscopy to measure a number of overtone bands. Our contribution in this area has been to record long path Fourier transform absorption spectra in the 16300–22800 cm^{-1} region (37). The most highly-excited vibrational state known to date is (007) with a band origin at 22625.50 cm^{-1} (37). Other experiments on HDO are the intracavity Fourier transform measurements of the 500 - 000 transition (38) as well as Russian intracavity measurements of (003) and (005) levels (39).

2. EXPERIMENTAL DETAILS

The hot HDO emission spectra were recorded on November 6, 1997 at the University of Waterloo with a Bruker IFS 120HR Fourier transform spectrometer. The spectrometer was operated with a KBr beamsplitter and either a Si:B or a HgCdTe detector. The spectra reported here in the 350 - 2200 cm^{-1} region were recorded in three pieces. The 350 - 750 cm^{-1} section used a liquid He-cooled Si:B detector and a cold longwave pass filter at 750 cm^{-1} . A separate cold bandpass filter was used to cover the 750 - 1300 cm^{-1} region. The 1200 - 2200 cm^{-1} region was recorded with a HgCdTe detector and an uncooled 2200 cm^{-1} longwave pass filter. Forty-five scans were co-added with Si:B detector and forty with the HgCdTe detector at a resolution of 0.01 cm^{-1} .

A KRS-5 window was used on the emission port of the spectrometer. The water vapor was heated in the center of a 1 m long, 5 cm diameter alumina tube sealed with cooled KRS-5 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 H₂O and D₂O liquids was used to provide the vapor. The thermal emission from the cell was focussed into the emission port of the spectrometer with an off-axis parabolic mirror. The lines were measured with the PC-Decomp program of Brault and have an estimated accuracy of $\pm 0.001 \text{ cm}^{-1}$ for strong unblended lines. The spectrum, however, was very dense with H₂O, D₂O and HDO lines present.

The three spectra analysed for this paper have lines in the regions 380-746, 750-1249 and 1250-2180 cm^{-1} . There were enough strong common lines in the two higher wavenumber spectra to put them on a common wavenumber scale and then calibrate them with the water lines reported in Polyansky et al. (40). Because of a lack of strong common lines between the two lower wavenumber regions, the lines in the 380–746 cm^{-1} region were just calibrated with our previous measurements (40) in this region. This means that in the 750–2190 cm^{-1} region our lines have a wavenumber scale that is in excellent agreement with that of Toth (41,42) but the 380–746 cm^{-1} region is on a

slightly different scale from Toth. Fortunately, this difference is less than 0.001 cm^{-1} , our estimated absolute accuracy.

3. LINE ASSIGNMENTS

A total of 22,106 lines were measured in the emission spectrum. Of course not all of these transitions correspond to HDO and before starting detailed analysis of these lines it was necessary to eliminate those due to H₂O and D₂O. The H₂O lines were identified by comparison with previously published (5,6) hot emission spectra. For D₂O similar comparisons were made with a ‘pure’ D₂O emission spectrum recorded in Waterloo which is yet to be fully analysed; in practice this D₂O spectrum contained approximately 10% HDO. As the intensities differ in the three regions of the HDO spectrum, these regions were analysed separately. 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. We identified 4155 H₂O lines (322 also belonging to HDO) and 5423 D₂O (447 also HDO). H₂O and D₂O lines are marked in the full linelist which is given in the supplementary data for this article.

Energy levels for the ground, (010), (020), (030), (100), (001) and (110) vibrational states of HDO with low J and K_a values have been given by Toth (18,19,21,22). These were used to conduct an initial analysis of the spectrum to identify ‘trivial’ assignments were both upper and lower energy levels were already known.

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 (9) 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. The 380 – 2190 cm^{-1} spectral region covers both pure rotational transitions of HDO, particularly with high J or K_a and the first bending fundamental, with a band origin at 1403.48 cm^{-1} , as well as associated hot bands.

Having eliminated trivial assignments and other isotopomers from our list of transitions, the unassigned lines were analysed using a computer program. Candidate transitions were identified using the variational linelist and then confirmed, or otherwise, by the presence, or not, of the appropriate combination difference transitions. In this way we were able to identify numerous new transitions involving known vibrational states and also to identify 190 transitions involving the (040) bending state.

The Partridge and Schwenke linelist (9) proved to be too restricted for the analysis of hot rotational levels. However they also provided (43) energy levels for higher states of HDO. These were used to provide estimates of frequencies for pure rotational transitions which were then used to seed a further search.

We have assigned 1146 pure HDO rotational transitions spanning all HDO states up to (110). 5085 transitions were assigned to bending transitions which involve a change of one quantum in the ν_2 mode. In addition 199 transitions were assigned to

assorted difference bands. It has already been found that these difference bands are common in the emission spectrum of hot H₂O (5,44). Table 1 gives a summary of all bands for which more than 10 transitions were assigned.

Experimental energy levels, which can be calculated by linking known energy levels and newly assigned transitions, are an important product of our analysis. This work has more than tripled the number of known energy levels for the states (000), (010), (020), (030) and (040). Tables 2 and 3 present energy levels for the first four of these states. The lowest *J* levels have been omitted from these tabulations as they have been well-determined previously (18,19). Our results for the previous unobserved (040) state are given in table 4.

Altogether we have assigned 6430 HDO transitions in the emission spectrum. This number represents approximately half the transitions which we identify as belonging to HDO. There is no doubt that many of the unassigned lines in the lower wavenumber portion of the spectrum belong to pure rotational transitions of vibrational states with excited stretching modes. Analysis of these states is best conducted in conjunction with analysis of associated vibrational transitions involving these stretching modes. Such transitions lie to somewhat higher frequency than the spectra reported here. An emission spectrum covering this region has been recorded in Waterloo and will be analysed together with the unassigned transitions remaining from the present study.

4. CONCLUSIONS

We present the first hot emission spectrum of HDO. This spectrum is very dense since it contains many lines belong to H₂O and D₂O as well as HDO. HDO lines have been identified by comparison with other hot emission spectra. The HDO transitions have been analysed resulting in the assignment of many hot pure rotational transitions, bending hot bands linking states up to the previously unobserved (040) bending state, as well as vibrational difference bands.

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