

The Visible and Near Ultraviolet Rotation–Vibration Spectrum of HOD

A. Jenouvrier,* M. F. Mérienne,* M. Carleer,† R. Colin,† A.-C. Vandaele,‡ P. F. Bernath,§
Oleg L. Polyansky,¶¹ and Jonathan Tennyson¶

**Spectrométrie Moléculaire et Atmosphérique, UFR Sciences, Moulin de la Housse, B.P. 1039, 51687 Reims Cedex 2, France;* †*Université Libre de Bruxelles, Service de Chimie Physique Moléculaire, CP 160/09, Av. F.D. Roosevelt 50, B-1050 Brussels, Belgium;* ‡*Institut d'Aéronomie Spatiale de Belgique, Av. Circulaire 3, B-1180 Brussels, Belgium;* §*Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1, and Department of Chemistry, University of Arizona, Tucson, Arizona 85721;* and ¶*Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom*

E-mail: mcarleer@ulb.ac.be, bernath@uwaterloo.ca, j.tennyson@ucl.ac.uk

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A Fourier transform spectrum has been recorded of a H₂O/D₂O vapor mixture in the wavenumber range 16,300 to 22,800 cm⁻¹ using a long path cell. 410 lines of HDO are assigned to the OH stretching overtone bands 5ν₃, 6ν₃ and 7ν₃ plus combination bands. Assignments for the 6ν₃ and 7ν₃ bands represent the first data for the 006 and 007 states and give band origins of 19,836.88 cm⁻¹ and 22,625.50 cm⁻¹, respectively. Rotational term values for these states are also obtained. © 2001 Academic Press

1. INTRODUCTION

The visible and near UV overtone spectrum of water vapor is relatively well known from the classic work of Camy-Peyret *et al.* (1) as well as the more extensive recent work of Carleer *et al.* (2) and Zobov *et al.* (3). The main application of this work is in atmospheric science because water vapor is the primary absorber of sunlight.

Work on the HOD isotopomer is much less extensive. For example, the 005 and 015 states at 16 899 and 18 208 cm⁻¹ (4–6) are the most highly excited known vibrational energy levels as compared to the 800 level of H₂O at 25 120 cm⁻¹ (3). Note that for HOD we adopt the traditional (but non-IUPAC) normal mode notation of ν₁ as the OD stretching mode, ν₂ as the bend, and ν₃ as the OH stretch.

Because H₂O can have such high abundance in the atmosphere, HOD is also an important atmospheric molecule. HOD can be readily observed in our atmosphere (7) and generally has a higher abundance than many well-known atmospheric molecules such as ozone. For example, if water has a mixing ratio of 1% (common in the troposphere) then HOD would have a volume mixing ratio of about 3 ppm, comparable to the important greenhouse gases CH₄ and N₂O.

The infrared spectra of HOD were first analyzed by Benedict *et al.* in 1956 (8). There has been much additional work since then, most notably by Toth and co-workers. The most recent and complete list of ground state energy levels is by Toth (9).

Supplementary data for this article are available on IDEAL (<http://www.idealibrary.com>) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

¹Permanent address: Institute of Applied Physics, Russian Academy of Science, Uljanov Street 46, Nizhni Novgorod, Russia 603024.

The visible and near infrared spectra of HOD have recently been studied by intracavity laser absorption spectroscopy in Grenoble. The 005 band (5) and the 015 band (6), the 004 band at 13 854 cm⁻¹ (10), 023 at 13 278 cm⁻¹ and 103 at 13 332 cm⁻¹ (11), 014 at 15,168 cm⁻¹ (12), and 024 at 16 456 cm⁻¹ (6) were the primary bands studied. Hu *et al.* (13) have measured the 400 band near 12 767 cm⁻¹ also by intracavity laser spectroscopy but they used a Fourier transform spectrometer rather than a spectrograph.

HOD differs from H₂O in that the three vibrational modes have very different frequencies and there are fewer interactions between modes. In particular, the strongest bands in the visible region are the overtones of the OH stretch and they behave like isolated states (5). This behavior has made HOD a popular molecule for bond-selective laser chemistry by dissociation (e.g., 14). The lines of the 004 band, for example, were first studied by photoacoustic and photodissociation spectroscopy (14) and then with a pulsed optical parametric oscillator (15).

While intracavity absorption spectroscopy and other laser-based techniques have a very high sensitivity, direct long path absorption experiments with a Fourier transform spectrometer (FTS) offer wide spectral coverage and a more precise wavenumber scale. We report here on our FTS measurements of the 005, 006, and 007 bands of HOD in the spectral region 16 300 to 22 800 cm⁻¹. There have been no previous measurements on HOD reported above 18 350 cm⁻¹.

2. EXPERIMENT

The HOD and H₂O experiments were carried out at the same time (2, 3). The measurements were made using the Bruker IFS

120 M high-resolution Fourier transform spectrometer of the Laboratoire de Chimie Physique Moléculaire (Université Libre de Bruxelles) coupled to the 50-m base length White-type multiple reflection absorption cell of the Groupe de Spectrométrie Moléculaire et Atmosphérique (Université de Reims). A 450-W xenon arc lamp was used as light source. Two detectors (a Si and a GaP diode) were used to record the spectral region from 10 000 to 30 000 cm^{-1} . The spectra were recorded at room temperature (18°C). We used 12 traversals through the cell, giving a total absorption path of 602.32 m. This path was chosen because it maximizes the signal-to-noise (S/N) ratio of the recorded spectra.

A nominal mixture of 42.5% H_2O and 57.5% D_2O was introduced into the cell at a total pressure of 9.8 Torr. From the relative amounts of H_2O and D_2O added to the cell, we estimate that the proportions of $\text{H}_2\text{O}/\text{HOD}/\text{D}_2\text{O}$ in the cell were about 19%, 47% and 34%, respectively. The spectra were recorded at a resolution of 0.06 cm^{-1} (15 cm maximum optical path difference) in two overlapping pieces. In the visible–near infrared region (13 100–22 300 cm^{-1}), the coaddition of some 2048 interferograms in a total recording time on the order of 12 h resulted in a S/N ratio of 3000. In the blue–near ultraviolet part (17 700–30 000 cm^{-1}) of the spectrum, the coaddition of 4096 interferograms (24 h of recording time) proved necessary to attain a S/N ratio of 2500. A third region was recorded in the near infrared (9 000–15 000 cm^{-1}), but the lines were mainly saturated and were not used.

Line positions and other parameters were measured in the near UV and visible spectra using a program called WSpectra developed by Carleer (16). Each line was fitted with a Voigt lineshape profile convolved by the instrumental function. After correction for the refractive index of air, the lines were calibrated by comparison with our previous water line positions (2, 3). Water lines were then removed from our linelists, leaving a list of 1381 lines. Tests with spectra which were recorded at different $\text{H}_2\text{O}/\text{D}_2\text{O}$ concentrations suggest that there are no D_2O lines in the region 18 000 to 23 000 cm^{-1} . The HOD line positions have an absolute accuracy of about 0.004 cm^{-1} . The resulting linelist is available electronically.

3. ANALYSIS

Significant advances have recently been made in the analysis of short wavelength spectra of water by using variational calculations (2, 3). These sophisticated calculations are required for water because of the strong polyad structure and, in particular, the large number of possible mixings within the higher polyads which make the use of methods based on effective hamiltonians difficult to apply. The spectrum of HOD is somewhat different as the isotopic substitution breaks the polyad structure and leads to a much better separation between the vibrational modes. This means that for high-lying states the bright OH stretching overtones are well separated from other vibrational modes and can be analyzed in isolation.

TABLE 1
Assigned Transitions in the $6\nu_3$ Band of HDO (Intensities Are Given in Arbitrary Units)

ν/cm^{-1}	Int	J'	K'_a	K'_c	J''	K''_a	K''_c
19905.0276	0.0173	5	1	4	4	1	3
19899.0979	0.0162	6	0	6	5	0	5
19894.9758	0.0116	5	2	3	4	2	2
19893.4305	0.0192	5	0	5	4	0	4
19893.2688	0.0173	4	1	3	3	1	2
19888.2104	0.0122	5	1	5	4	1	4
19886.3719	0.0220	4	0	4	3	0	3
19882.4303	0.0134	5	2	4	4	2	3
19879.3349	0.0173	3	1	2	2	1	1
19879.2615	0.0202	4	1	4	3	1	3
19877.9379	0.0128	4	2	2	3	2	1
19877.2228	0.0259	3	0	3	2	0	2
19870.9360	0.0126	4	2	3	3	2	2
19869.0122	0.0185	3	1	3	2	1	2
19865.5737	0.0162	2	0	2	1	0	1
19864.0450	0.0123	2	1	1	1	1	0
19861.0568	0.0091	3	2	1	2	2	0
19858.1202	0.0097	3	2	2	2	2	1
19857.4805	0.0118	2	1	2	1	1	1
19851.8494	0.0098	1	0	1	0	0	0
19845.5662	0.0053	4	3	2	3	3	1
19838.4211	0.0061	2	1	1	2	1	2
19833.7071	0.0122	1	1	0	1	1	1
19827.9329	0.0115	1	1	1	1	1	0
19823.1772	0.0032	5	2	3	5	2	4
19821.3695	0.0088	0	0	0	1	0	1
19821.1100	0.0062	2	1	2	2	1	1
19817.9723	0.0055	4	2	2	4	2	3
19814.9192	0.0106	3	2	1	3	2	2
19813.9643	0.0175	2	2	0	2	2	1
19812.9285	0.0176	2	2	1	2	2	0
19810.6848	0.0037	3	1	3	3	1	2
19810.0101	0.0090	3	2	2	3	2	1
19805.6792	0.0134	1	0	1	2	0	2
19804.4783	0.0067	4	2	3	4	2	2
19802.3121	0.0110	1	1	1	2	1	2
19797.3332	0.0105	1	1	0	2	1	1
19789.7509	0.0177	2	0	2	3	0	3
19786.9005	0.0141	2	1	2	3	1	3
19784.7329	0.0153	3	3	0	3	3	1
19784.6106	0.0143	3	3	1	3	3	0
19782.9099	0.0090	4	3	2	4	3	1
19780.0863	0.0145	2	1	1	3	1	2
19773.2313	0.0166	3	0	3	4	0	4
19770.7577	0.0161	3	1	3	4	1	4
19766.7580	0.0248	2	2	1	3	2	2
19765.8269	0.0077	2	2	0	3	2	1
19762.5422	0.0145	3	1	2	4	1	3
19755.7567	0.0150	4	0	4	5	0	5
19753.7888	0.0145	4	1	4	5	1	5
19750.0327	0.0099	3	2	2	4	2	3
19748.4875	0.0109	3	2	1	4	2	2
19744.4954	0.0118	4	1	3	5	1	4
19737.2698	0.0126	5	0	5	6	0	6
19735.9791	0.0074	5	1	5	6	1	6
19732.6874	0.0085	4	2	3	5	2	4
19731.0133	0.0105	4	2	2	5	2	3
19725.5045	0.0092	5	1	4	6	1	5
19722.1149	0.0033	3	3	1	4	3	2
19717.8861	0.0098	6	0	6	7	0	7
19716.9998	0.0074	6	1	6	7	1	7
19714.6006	0.0076	5	2	4	6	2	5
19713.2623	0.0081	5	2	3	6	2	4

Our initial analysis concentrated on assigning transitions to states of $v_3 = 5, 6,$ and 7 by extrapolating rotational constants from lower v_3 overtone states. This method allowed the assignment of many low J transitions. During the course of this work Schwenke (17) updated the previous variational linelist for HOD (18). Use of this linelist confirmed many of the previous assignments and suggest some candidate transitions with higher rotational excitation. However, this linelist does not extend above $20,000 \text{ cm}^{-1}$.

A second approach was then tested. First a computer program was used to identify all possible transitions between known energy levels ('trivial assignments'). For this purpose we used both our newly-determined energy levels, and those obtained previously (5, 6). Another program was then written which identified possible assignments based on combination differences. This produced a large number of possible assignments which were then reduced to a manageable list of candidates using intensity considerations. Further assignments were made using the same procedure used to confirm the original assignments. However, many possible candidates could not be confirmed in this way and must await further work, probably using an improved linelist.

A total of 410 lines have been assigned to HDO including assignments obtained to the 015 and 024 combination bands.

TABLE 2
Assigned Transitions in the $7\nu_3$ Band of HDO (Intensities Are Given in Arbitrary Units)

ν/cm^{-1}	Int	J'	K'_a	K'_c	J''	K''_a	K''_c
22679.6104	0.0022	5	0	5	4	0	4
22674.0248	0.0018	5	1	5	4	1	4
22673.4218	0.0022	4	0	4	3	0	3
22666.7297	0.0016	3	1	2	2	1	1
22665.9459	0.0023	4	1	4	3	1	3
22665.0010	0.0025	3	0	3	2	0	2
22656.2027	0.0021	3	1	3	2	1	2
22653.8612	0.0019	2	0	2	1	0	1
22640.3938	0.0014	1	0	1	0	0	0
22621.5309	0.0013	1	1	0	1	1	1
22615.7217	0.0014	1	1	1	1	1	0
22609.9948	0.0015	0	0	0	1	0	1
22599.4347	0.0018	2	2	0	2	2	1
22598.3256	0.0020	2	2	1	2	2	0
22594.2170	0.0017	1	0	1	2	0	2
22590.0858	0.0018	1	1	1	2	1	2
22585.1591	0.0014	1	1	0	2	1	1
22578.0408	0.0023	2	0	2	3	0	3
22576.1574	0.0024	2	1	2	3	1	3
22566.2672	0.0016	3	3	0	3	3	1
22566.1165	0.0017	3	3	1	3	3	0
22561.0141	0.0022	3	0	3	4	0	4
22557.9103	0.0000	3	1	3	4	1	4
22551.3050	0.0009	2	2	0	3	2	1
22549.9357	0.0018	3	1	2	4	1	3
22542.8093	0.0015	4	0	4	5	0	5
22540.4696	0.0020	4	1	4	5	1	5
22523.4549	0.0018	5	0	5	6	0	6
22521.7825	0.0013	5	1	5	6	1	6
22503.6648	0.0009	3	3	1	4	3	2

TABLE 3
HDO Vibration-Rotation Energy Levels in cm^{-1} Derived Using Experimental Data for the $6\nu_3$ and $7\nu_3$ Vibrational States ('N' Gives the Number of Transitions Observed at a Particular Level)

$J K_a K_c$	(006)	N	(007)	N
0 0 0	19836.8777	1	22625.5030	1
1 0 1	19851.8509	2	22640.3919	2
1 1 1	19860.4341	2	22648.2154	2
1 1 0	19863.5167	2	22651.3416	2
2 0 2	19881.0814	2	22669.3701	2
2 1 2	19887.2916	3	22676.5482	1
2 1 1	19896.5456	3		
2 2 1	19922.1723	2	22707.5946	1
2 2 0	19922.8911	2	22708.3653	2
3 0 3	19923.3916	2	22711.1721	2
3 1 3	19927.1417	3	22714.3111	2
3 1 2	19945.5225	2	22732.9166	2
3 2 2	19967.0652	3		
3 2 1	19970.3192	3		
3 3 1	20017.6318	2	22799.1598	2
3 3 0	20017.7565	1	22799.2908	1
4 0 4	19977.7023	2	22764.7536	2
4 1 4	19979.6529	2	22766.3355	2
4 1 3	20009.7307	2		
4 2 3	20026.3211	3		
4 2 2	20035.0083	3		
4 3 2	20078.5885	2		
5 0 5	20043.5854	2	22829.7679	2
5 1 5	20044.5936	2	22830.4025	2
5 1 4	20088.0112	2		
5 2 4	20099.4740	2		
5 2 3	20116.8121	3		
6 0 6	20121.0456	2		

Approximately 150 of these assignments were taken from previous studies (5, 6). Tables 1 and 2 present our newly assigned transitions for the $6\nu_3$ and $7\nu_3$ bands, respectively. These tables also give relative intensities for the different transitions. These assignments, as well as those for the $5\nu_3$ state and for the combination bands, are given as part of the electronic linelist. The assignments to 005, which were largely performed prior to us becoming aware of the work of Bertseva *et al.* (5) and therefore independent of it, were found to be in complete agreement. This is probably a manifestation of the fact that HDO is, compared to water, a straightforward system with relatively few vibrational perturbations. Although Bertseva *et al.*'s coverage of the 005 band is greater than ours we still have some lines and energy levels not reported in that work including transitions to the 14_{114} rotational state.

Our new transitions can be combined with the term values obtained by Toth (9) to give energy levels for the vibrationally excited states. Table 3 presents our new levels for the $6\nu_3$ and $7\nu_3$ vibrational states. Levels whose energies have been obtained by more than one transition, as denoted by an N value greater than one in the table, have been confirmed by combination differences. In practice we believe even the values for levels with $N = 1$ are secure. Our energy level calculations show that the

band origin for the $6\nu_3$ state is at $19\,836.88\text{ cm}^{-1}$ and that for the $7\nu_3$ vibrational state is at $22\,625.50\text{ cm}^{-1}$.

4. CONCLUSIONS

A long path length Fourier transform spectrum has been recorded for a $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture which yielded many lines of HDO in the $5\nu_3$, $6\nu_3$, and $7\nu_3$ vibrational bands plus combination bands. Assignments in the $6\nu_3$ and $7\nu_3$ bands represent the first data for these highly excited OH stretching states.

The experimental study yielded 1381 lines over a 6000 cm^{-1} region. So far we have assigned 410 lines definitely to HDO, largely OH overtone stretching transitions. Further progress on the assignment of HDO lines in the spectra must await the calculation of a variational linelist valid over a more extended energy range. Such calculations are significantly more expensive than the corresponding calculations on water because of the loss of symmetry in HDO and also the increase in the number of states caused by deuteration. However the new data obtained here, particularly the vibrational band origins, form important input for spectroscopically determined potentials which, in turn, can be used to compute extensive and reliable linelists. Work on this aspect of the problem is in progress at University College London.

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