

The visible and near ultraviolet rotation-vibration spectrum of HOD

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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 $5\nu_3$, $6\nu_3$ and $7\nu_3$ plus combination bands. Assignments for the $6\nu_3$ and $7\nu_3$ 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.

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 cm⁻¹ 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 for HOD we adopt the traditional (but non-IUPAC) normal mode notation of ν_1 as the OD stretching mode, ν_2 as the bend and ν_3 as the OH stretch.

Because H₂O can have such a 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, Gailar and Plyler 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).

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

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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 H_2O 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 photo-acoustic 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 a 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 16,300 – 22,800 cm^{-1} spectral region. There have been no previous measurements on HOD reported above 18,350 cm^{-1} .

2. EXPERIMENT

The HOD and H_2O 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 in 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 of 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 18,000 – 23,000 cm^{-1} region. 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.

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 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. 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 of 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.

ACKNOWLEDGMENTS

This work was supported by the Prime Minister's Office-Federal Office for Scientific, Technical and Cultural Affairs and the Fonds National de la Recherche Scientifique (Belgium). Support was provided by the Centre National de Recherche Scientifique and the Institut National des Sciences de l'Univers through the Programme National de Chimie Atmospherique (contract 98N51/0324) (France). The work of O.L.P. was supported in part by the Russian Fund for Fundamental Studies. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). Acknowledgment is made to the Petroleum Research Fund for partial support of this work. Some support was also provided by the NASA Labo-

ratory Astrophysics Program, the UK Engineering and Science Research Council and the UK Natural Environment Research Council.

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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

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 to 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		