$3\nu_3$ BAND OF THE $HD^{16}O$ MOLECULE

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The absorption spectrum of $HD^{16}O$ in the region 10280 ... 10770 cm^{-1} was recorded using an intracavity spectrometer with an LiF: F_2^+ color-center laser. To identify the lines the energy levels of the 003 state were determined, the inverse problem was solved, and the rotational and centrifugal constants were determined.

High-resolution spectra of the $HD^{16}O$ molecule are of interest for a number of reasons. First, $HD^{16}O$ vapor is present in the atmosphere and makes a significant contribution to the absorption in the middle-IR region. Second, the vibrational-rotational spectra of the isotopic modifications of water give additional information necessary for reconstructing the parameters of the intramolecular potential function and the dipole moment of the molecule. Finally, the $HD^{16}O$ molecule, like other isotopic modifications of water, light asymmetric tops whose energy spectrum has a number of peculiarities, and it is necessary to study its highly excited rotational and vibrational states in order to analyze theoretically the effect of intramolecular interactions on the formation of the spectrum. The absorption spectra of $HD^{16}O$ have been studied in detail in the microwave, far- and mid-IR regions, and the energy levels and the rotational and centrifugal constants are presented in Refs. 1–10 for states whose energy is less than 9300 cm^{-1}. In this paper we present the results of the recording and analysis of the absorption spectrum near 0.94 μm.

1. The absorption spectra were recorded using an intracavity spectrometer based on an LiF: F_2^+ laser. The laser cavity consisted of a flat mirror (reflection coefficient of 90%) and a spherical mirror (reflection coefficient of 99.9%) and a dispersion prism. The active element consisted of a 4×10×10 mm LiF: F_2^+ crystal, and the overall length of the resonator was equal to 60 cm. The LiF: F_2^+ laser was pumped in a longitudinal arrangement by ruby laser radiation (the duration of quasi continuous lasing was equal to 900 μs and the energy was equal to 3 J). The pump radiation was focused on the ’crystal with the help of a lens with a focal lehgth of 20 cm. Quasi continuous lasing-with a duration of 400 μs was obtained; this ensures a sensitivity of 10^{-7} cm^{-1}. An evacuated cavity was employed in order to eliminate absorption in atmospheric lines.

The lasing spectrum of the laser was recorded with a spectrograph, assembled based on a UF-90 self-collimation camera and a diffraction grating with 300 lines/mm. The inverse linear- dispersion was equal to 0. 1 nm/mm and the spectral resolution was equal to 0.05 cm^{-1}.

First the absorption spectra of $H_2^{16}O$ and $D_2^{16}O$ were recorded in the region 0.94 μm and interpreted. The HDO molecule cannot be recorded independently, since an equilibrium mixture of three isotopes of water vapor is always present:

$$H_2O + D_2O \rightleftarrows 2HDO.$$

For this reason we recorded the absorption spectrum of an equilibrium mixture of H_2O, D_2O, and HDO the (total pressure was equal to 19 torr and the temperature was equal to 296 K), and the absorption lines of the main modification present in the spectrum were employed as the reference lines, relative to which the position of the centers of the HDO lines was measured with an error of not less 0.05 cm^{-1}.

2. Analysis of the spectrum identification of the lines were performed as follows. First the integral intensities, the band centers, and the rotational constants of $HD^{16}O$ and $D_2^{16}O$ were determined, for the bands falling into the range studied. The isotopic ratios of Ref. 11, the estimates of the anharmonic constants of Ref. 12, the vibrational-rotational constants constants of Ref. 13, and the integrated intensities of some bands of $H_2^{16}O$ were employed. To calculate the band centers of .the asymmetric modification the inverse vibrational problem was solved first based on experimental data published for 13 bands using the method described in Ref. 12. To make a preliminary calculation of the rotational constants of $HD^{16}O$ the published data on the vibrational-rotational levels of the molecules were analyzed. For a number of states the rotational constants were not determined; in this case the inverse problem was solved with levels up to $J \le 3$ and the values of the vibrational energy and the constants A, B, C, and Δ_k were found. Next, the vibrational-rotational constants, determining the

dependence of the rotational constants on the vibrational quantum numbers, were- found by the least-squares method, as dpne in Ref. 13 for the main modification. The values found were employed to determine the spectroscopic parameters of HD^{16}O.

The results of preliminary calculations made it possible to determine the position and the relative strengths of lines in the spectrum. The lines of four HD^{16}O fall into the range studied 10,280 ... 10,770 cm^{-1}. These are transitions from the ground state to the states 003, 211, 131, and 051. The absorption lines of D$_2^{16}$O can belong to three bands, corresponding to transitions on 103, 202, and 301. In addition, lines in the bands $\nu_1 + 2\nu_3$, $2\nu_1 + \nu_3$, and $\nu_1 + 2\nu_2 + \nu_3$ of the main isotope fall into the same range. The strongest band of the D$_2^{16}$O molecule in the spectral range indicated is the band $3\nu_1 + \nu_3$ centered at 10,371 cm^{-1}; the $3\nu_1 + \nu_3$ band is an order of magnitude weaker and the $2\nu_1 + 2\nu_3$ band is still weaker, The strongest bands of HD^{16}O are $3\nu_3$ centered at 10,623 cm^{-1}, and $2\nu_1 + \nu_2 + \nu_3$ near 10,399 cm^{-1}; the lines of the bands $\nu_1 + 3\nu_2 + \nu_3$ and $5\nu_2 + \nu_3$ are very weak and apparently are not manifested in the spectrum. Thus in the spectra of the samples studied in the range 10,280 ... 10,770 cm^{-1} the lines of the $3\nu_3$ band of HD^{16}O should be primarily interpreted.

The lines were identified by the method of combination differences of the lower state. The energy levels of the ground vibrational state were calculated from the spectroscopic parameters taken from Ref. 1. At the time the lines were identified the inverse problem was solved, and the rotational and centrifugal constants of the 003 state of HD^{16}O were refined; this made it possible to determine more accurately the position of the lines with large angular momentum quantum numbers in the spectrum and to control the referencing of the lines. The energy levels as the arithmetic mean over several lines and the rms error were determined from the results of identification.

3. As a result of the analysis of the spectrum 100 energy levels were found for the 003 state of HD^{16}O, corresponding to $J \le 15$ and $K_a \le 6$, with an accuracy ranging from 0.01 to 0.06 cm^{-1}, and for most levels the rms error does not exceed 0.03 cm^{-1}. As a rule, the level was determined from three to four lines; in separate cases six lines were employed. Only those absorption lines of HD^{16}O whose centers do not overlap with the lines of the main isotopic modification were employed.

Preliminary analysis showed that the 003 vibrational state is isolated and the possible resonances can be neglected. Indeed, the 211 and 131 states of the molecule which have the closest vibrational energy (split from 003 by not more than 150 cm^{-1}) give a large total change in the vibrational quantum numbers, so that the leading terms in the off-diagonal matrix element, which could give rise to a resonance, are determined by fifth- and sixth-order anharmonic constants. At the same time the matrix elements corresponding to Cariolis and Fermi resonances are coupled with the states under study, which are split by 700 and more inverse centimeters. As a result of this the rotational and centrifugal constants were determined with the help of the nonresonance model — the Watson Hamiltonian:[14]

$$H = E + \left[A - \frac{B+C}{2}\right] J_z^2 + \frac{B+C}{2} J^2 + \frac{B-C}{2} J_{xy}^2 - \Delta_k J_z^4 -$$

$$- \Delta_{Jk} J^2 J_z^2 - \Delta_J \, J^2)^2 - \delta_k \left\{J_z^2, J_{xy}^2\right\} - 2\delta_J J^2 J_{xy}^2 + H_k J_z^6 +$$

$$+ H_{kJ}{}^2 J_z^4 + H_{Jk} (J^2)^2 J_z^2 + H_J (J^2)^3 + h_k \left\{J_z^4, J_{xy}^2\right\},$$

where

$$J^2 = J_x^2 + J_y^2 + J_z^2; \quad J_{xy}^2 = J_x^2 - J_y^2;$$

$$\{A, B\} = AB + BA.$$

The parameters of the Hamiltonian which were obtained by solving the inverse problem as well as the 68% confidence intervals are given in Table I.

TABLE I

The rotational and centrifugal 003 state of HD^{16}O *(in cm^{-1}).*

Parameter	Values of the constants	Confidence interval
E	$10631{,}587_{29}$	0,021
A	$20{,}5571_{15}$	0,0057
B	$9{,}0647_{63}$	0,0014
C	$6{,}1682_{54}$	0,0010
$\Delta_k \cdot 10^2$	$6{,}815_{92}$	0,039
$\Delta_{Jk} \cdot 10^3$	$1{,}01_{67}$	0,11
$\Delta_J \cdot 10^4$	$3{,}371_{03}$	0,087
$\delta_k \cdot 10^3$	$3{,}508_{56}$	0,087
$\delta_J \cdot 10^4$	$1{,}023_{85}$	0,044
$H_k \cdot 10^3$	$4{,}5671_{42}$	0,0075
$H_{kJ} \cdot 10^6$	$-7{,}1_{89}$	3,3
$H_{Jk} \cdot 10^6$	$2{,}81_{43}$	0,50
$H_J \cdot 10^8$	$8{,}7_{78}$	2,7
$h_k \cdot 10^4$	$2{,}387_{36}$	0,075

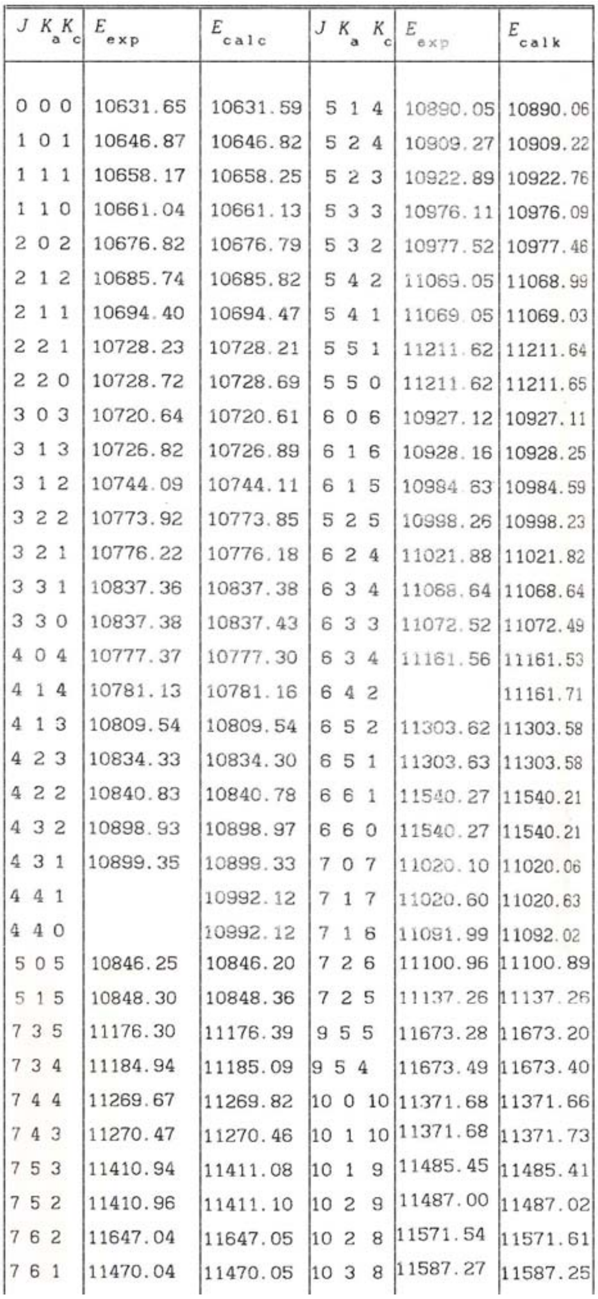
Table II gives the energy levels found from the transition frequencies and computed with the parameters of the equation. The first three columns of Table II give the quantum numbers J, K_a, and K_c, the fourth column gives the experimental levels, and the last column gives the computed values. One can see from the data given in Table II that the agreement between the computed values of the energy levels and the values found from the spectrum is satisfactory — the standard deviation is equal to 0.06 cm^{-1}. On the whole the following relations characterize the accuracy with which the experimental levels are reproduced ($\sigma = |E_{\text{esp}} - E_{\text{comp}}|$):

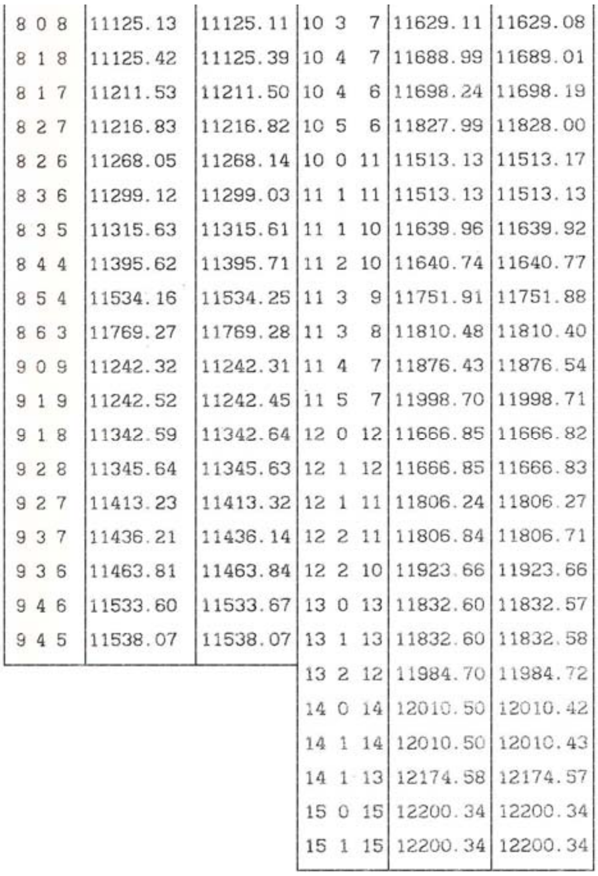
$\sigma \leq 0.03$ cm^{-1} for 49.1% of all the levels
$0.03 \leq \sigma \leq 0.06$ " " 22.3% " "
$0.03 < \sigma \leq 0.09$ " " 22.3% " "
$0.09 < \sigma$ " " 6.3% " "

The data in Tables I and II represent the energy structure of the highest of the known vibrational states of $HD^{16}O$.

TABLE II

The energy levels of the 003 state of $HD^{16}O$ *(in* cm^{-1}*).*





J K_a K_c	E_{exp}	E_{calc}	J K_a K_c	E_{exp}	E_{calk}
0 0 0	10631.65	10631.59	5 1 4	10890.05	10890.06
1 0 1	10646.87	10646.82	5 2 4	10909.27	10909.22
1 1 1	10658.17	10658.25	5 2 3	10922.89	10922.76
1 1 0	10661.04	10661.13	5 3 3	10976.11	10976.09
2 0 2	10676.82	10676.79	5 3 2	10977.52	10977.46
2 1 2	10685.74	10685.82	5 4 2	11069.05	11068.99
2 1 1	10694.40	10694.47	5 4 1	11069.05	11069.03
2 2 1	10728.23	10728.21	5 5 1	11211.62	11211.64
2 2 0	10728.72	10728.69	5 5 0	11211.62	11211.65
3 0 3	10720.64	10720.61	6 0 6	10927.12	10927.11
3 1 3	10726.82	10726.89	6 1 6	10928.16	10928.25
3 1 2	10744.09	10744.11	6 1 5	10984.63	10984.59
3 2 2	10773.92	10773.85	5 2 5	10998.26	10998.23
3 2 1	10776.22	10776.18	6 2 4	11021.88	11021.82
3 3 1	10837.36	10837.38	6 3 4	11068.64	11068.64
3 3 0	10837.38	10837.43	6 3 3	11072.52	11072.49
4 0 4	10777.37	10777.30	6 3 4	11161.56	11161.53
4 1 4	10781.13	10781.16	6 4 2		11161.71
4 1 3	10809.54	10809.54	6 5 2	11303.62	11303.58
4 2 3	10834.33	10834.30	6 5 1	11303.63	11303.58
4 2 2	10840.83	10840.78	6 6 1	11540.27	11540.21
4 3 2	10898.93	10898.97	6 6 0	11540.27	11540.21
4 3 1	10899.35	10899.33	7 0 7	11020.10	11020.06
4 4 1		10992.12	7 1 7	11020.60	11020.63
4 4 0		10992.12	7 1 6	11091.99	11092.02
5 0 5	10846.25	10846.20	7 2 6	11100.96	11100.89
5 1 5	10848.30	10848.36	7 2 5	11137.26	11137.26
7 3 5	11176.30	11176.39	9 5 5	11673.28	11673.20
7 3 4	11184.94	11185.09	9 5 4	11673.49	11673.40
7 4 4	11269.67	11269.82	10 0 10	11371.68	11371.66
7 4 3	11270.47	11270.46	10 1 10	11371.68	11371.73
7 5 3	11410.94	11411.08	10 1 9	11485.45	11485.41
7 5 2	11410.96	11411.10	10 2 9	11487.00	11487.02
7 6 2	11647.04	11647.05	10 2 8	11571.54	11571.61
7 6 1	11470.04	11470.05	10 3 8	11587.27	11587.25
8 0 8	11125.13	11125.11	10 3 7	11629.11	11629.08
8 1 8	11125.42	11125.39	10 4 7	11688.99	11689.01
8 1 7	11211.53	11211.50	10 4 6	11698.24	11698.19
8 2 7	11216.83	11216.82	10 5 6	11827.99	11828.00
8 2 6	11268.05	11268.14	10 0 11	11513.13	11513.17
8 3 6	11299.12	11299.03	11 1 11	11513.13	11513.13
8 3 5	11315.63	11315.61	11 1 10	11639.96	11639.92
8 4 4	11395.62	11395.71	11 2 10	11640.74	11640.77
8 5 4	11534.16	11534.25	11 3 9	11751.91	11751.88
8 6 3	11769.27	11769.28	11 3 8	11810.48	11810.40
9 0 9	11242.32	11242.31	11 4 7	11876.43	11876.54
9 1 9	11242.52	11242.45	11 5 7	11998.70	11998.71
9 1 8	11342.59	11342.64	12 0 12	11666.85	11666.82
9 2 8	11345.64	11345.63	12 1 12	11666.85	11666.83
9 2 7	11413.23	11413.32	12 1 11	11806.24	11806.27
9 3 7	11436.21	11436.14	12 2 11	11806.84	11806.71
9 3 6	11463.81	11463.84	12 2 10	11923.66	11923.66
9 4 6	11533.60	11533.67	13 0 13	11832.60	11832.57
9 4 5	11538.07	11538.07	13 1 13	11832.60	11832.58
			13 2 12	11984.70	11984.72
			14 0 14	12010.50	12010.42
			14 1 14	12010.50	12010.43
			14 1 13	12174.58	12174.57
			15 0 15	12200.34	12200.34
			15 1 15	12200.34	12200.34

REFERENCES

1. J.K. Messer, F.C. De Lucia, and P. Helminger, J. Mol. Spectrosc., **105**. 139 (1984).
2. W.S. Benedict, N. Gailar, and E.K. Plyler, J. Chem. Phys. **24**, 1139 (1959).
3. J.W.S. Johns, J. Opt. Soc. Am., **B2**. 1340 (1985).
4. R.A. Toth, V.D. Gupta, and J.W. Brault, Appl. Opt. **21**. 3337 (1982).
5. R.A. Toth and J.W. Brault, Appl. Opt. **22**, 908 (1983).
6. A. Perrin, J.-M. Flaud, and C. Camy-Peyret, J. Mol. Spectrosc., **112**. 153 (1985).
7. A. Perrin, C. Camy-Peyret and J.-M. Flaud, Can. J. Phys. **64**, 736 (1986).
8. A.D. Bykov, V.P. Lopasov, Yu.S. Makushkin, et al., J. Mol. Spectrosc. **94**, 1 (1984).
9. A.D. Bykov, Yu.S. Makushkin V.I. Serdyukov, et al., J Mol. Spectrosc. **105**, 397 (1982).
10. N. Papineau, C. Camy-Peyret, and J.-M. Flaud, J. Mol. Spectrosc., **92**, 451 (1982).
11. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov *Isotopic Substitution in Polyatomic Molecules* (Nauka, Novosibirsk, 1985).
12. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, Opt. i Spektrosk, **56**, 425 (1984).
13. V.N. Bryukhanov, A.D. Bykov, Yu.S. Makushkin, et al., Opt. i Spektrosk. **54**, 916 (1983).
14. J.K.G. Watson, J. Chem. Phys., **46**, 1935 (1967).