# The $4V_{OH}$ Absorption Spectrum of HDO

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The absorption spectrum of HDO was recorded by intracavity laser absorption spectroscopy in the 13 560–14 050 cm<sup>-1</sup> spectral region. Among 437 lines attributed to HDO, 399 were assigned to the  $4\nu_3$  highly excited overtone transition. One hundred twenty-nine experimental energy levels were derived from the spectrum identification with rotational quantum numbers *J* as high as 16 and  $K_a$  as high as 7. The (004) vibrational state of HDO was found to be nearly isolated. Rotational and centrifugal distortion parameters of the effective rotational Hamiltonian in the Pade–Borel approximants form, retrieved from the fitting, allow the reproduction of the experimental energy levels with the root-mean-square deviation of 0.012 cm<sup>-1</sup>, close to the experimental accuracy. Some rotational energy levels of the (004) state seem to be slightly perturbed by local resonances with the (052) highly excited bending state. The resonance mixing was found to be large enough to give rise to seven  $5\nu_2 + 2\nu_3$  transitions, but otherwise too weak to be observable. The maximum difference between the derived experimental energy levels and the recent high accuracy *ab initio* predictions (H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618–4639 (1997)) is  $-2.7 \text{ cm}^{-1}$ . @ 1999 Academic Press

# 1. INTRODUCTION

The HDO molecule is a nonsymmetric isotopomer of H<sub>2</sub>O with the symmetry reduced from  $C_{2v}$  to  $C_s$ . The ratio between the harmonic frequencies of HDO differs significantly from that of H<sub>2</sub>O resulting in different intramolecular dynamics as compared to the parent molecule. In particular, there is a large difference of about 1000 cm<sup>-1</sup> between  $\omega_1$  and  $\omega_3$  harmonic frequencies that leads to a quenching of the Coriolis-type resonance and the existence of a well-isolated N $\nu_3$  band sequence up to  $5\nu_3$  at 16 920 cm<sup>-1</sup> (1). (Note that, contrary to the recommendations of IUPAC, we use the traditional labeling of the stretching vibration with  $v_1$  and  $v_3$  standing for the OD and OH stretching, respectively.) On the other hand, an unusually strong high-order anharmonic interaction which couples (210) and (050) states of HDO was found to take place, as reported in (2), giving rise to relatively strong  $5\nu_2$  transitions, whereas the conventional Fermi-type resonance between (210) and (130) states was estimated to be rather weak.

Highly excited stretching vibrations of HDO are also of special interest in connection with the study of state-to-state molecular photodissociation dynamics (see for example Refs. (3, 4) and references therein). Substitution of a hydrogen atom by deuterium destroys the degeneracy of the local-mode stretching vibrational states and leads to the localization of the vibrational excitation on one of the two bonds, resulting in selective cleavage of the excited bond.

Rotationally resolved OD and OH stretching vibrations of the HDO molecule were recently investigated both in the near-infrared  $(2\nu_3 \ (5, \ 6), \ 3\nu_3 \ (1, \ 4), \ and \ 2\nu_1 \ (7))$  and in the visible range  $(4\nu_3 \ (3), 5\nu_3 \ (1), \ and \ 5\nu_1 \ (8))$  by optoacoustic and intracavity laser absorption (ICLAS) spectroscopy. It follows from these studies that all analyzed states can be treated as isolated or slightly perturbed states. Nevertheless, transitions on the [110] energy level of the highly excited (170) state were assigned in (8) as resulting from an intensity borrowing through weak coupling with relatively strong  $5\nu_1$  resonant line-partners. Weak coupling of (011) and (200) vibrational states produces a considerable (up to one order of magnitude) increase in the  $2\nu_1$  transitions involving perturbed energy levels (7).

In the case of the (004) state under consideration, one can expect local perturbations of the energy levels due to coupling with the highly excited (052) bending state. The central part of this band recorded by the optoacoustic technique (3) was analyzed by Fair *et al.* We present hereafter the analysis of the same band recorded by ICLAS with an increased sensitivity.

#### 2. EXPERIMENTAL DETAILS

The experimental apparatus for ICLAS was previously described in detail (9). The technical details and a very recent review of the results obtained by ICLAS in the field of overtone spectroscopy and optical diagnostics will be found in Ref. (10) together with a systematic comparison with other highly sensitive laser techniques. In the current experiment, we used a standard standing-wave dye-laser cavity with a 50-cm cell inserted in the long arm of the cavity. A Pyrydine1 dye solution was used to record the spectrum between 13 560 and 14 050 cm<sup>-1</sup>. The intracavity sample cell was filled with a 1:1 mixture



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of H<sub>2</sub>O and D<sub>2</sub>O at a pressure of 20 Torr (145 hPa) just below the vapor pressure at room temperature (25°C). This procedure is assumed to lead to a mixture of H<sub>2</sub>O:HDO:D<sub>2</sub>O in the proportion 1:2:1. The spectra were obtained with generation times up to 100  $\mu$ s corresponding to equivalent absorption path lengths of up to 15 km.

The data acquisition system was upgraded with a 3754 pixels CCD which records the laser spectrum dispersed by the grating spectrograph. This system allows the recording of a slice of 15 cm<sup>-1</sup> of the laser spectrum with the higher resolution configuration of the spectrograph (resolving power 8 imes $10^{\circ}$ ). The spectral resolution of the high-resolving grating spectrograph dispersing the laser spectrum is about  $0.02 \text{ cm}^{-1}$ . a factor of 2 smaller than the Doppler broadening  $(0.04 \text{ cm}^{-1})$ FWHM). The wavenumber calibration procedure consists, first, of correcting the nonlinearity of the spectrograph dispersion by using an étalon inserted into the laser beam giving sharp fringes equidistant in frequency. The pixel to wavenumber dependence was then linearized for each spectrograph position and absolutely calibrated by the use of two reference lines of H<sub>2</sub>O (11) appearing superimposed on the HDO spectrum. We estimate our wavenumber calibration to be accurate to within 0.01 cm<sup>-1</sup> as will be confirmed by the ground state combination differences provided by the forthcoming rotational analysis.

## 3. THEORY AND RESULTS

Among 1244 measured absorption lines in the 13 560– 14 050 cm<sup>-1</sup> spectral region, 437 were attributed to HDO transitions. The spectrum identification was performed using a computer program based on the pattern recognition theory (12). The initial set of rotational and centrifugal distortion constants was derived from the fitting of the (004) state lowlying rovibrational energy levels provided by accurate *ab initio* calculations (13).

For identification purposes an estimation of the experimental relative intensities was obtained for each observed line. Approximate dipole-moment parameters for the a- and b-type  $4\nu_3$  transitions were derived in the conventional manner (14) from the fitting to several tens of well-resolved isolated lines providing reasonable predictions of the intensities of all analyzed lines. The assignment process was done in parallel with refinement of the rotational parameters as the data set was increased. Finally, it was possible to assign even weak single lines relying on accurate line positions and intensity predictions.

As a result of the analysis, 399 among the 437 HDO lines were assigned as belonging to the  $4\nu_3$  band, 7 lines were attributed to  $5\nu_2 + 2\nu_3$  band transitions, borrowing their intensities through resonance coupling. The list of the HDO lines in the spectral region of interest is presented in Table 1. To give some idea of the absolute intensities of the observed lines, we used Partridge and Schwenke (13) intensity predictions related to pure HDO at 296 K to normalize our relative calculated intensities to the total predicted band intensity. The deviation in the normalized intensity values exceeds 60% for only 37 lines with an average agreement with the Ref. (13) data being of 24%. Our normalized calculated intensities, as well as those predicted in Ref. (13), are given in Table 1. It is worth mentioning that for the  $2\nu_2$  band transitions, intensity estimations (13) were found to be very accurate (within 4.5%) (6).

About 30 HDO lines were found to be partially blended by  $H_2O$  lines. They are marked by the label "b" in Table 1. Unassigned lines which represent only 7% of all lines are also given in Table 1 with an experimental intensity estimation. Some strong HDO lines are absent in our line list due to unrecoverable overlapping with strong H<sub>2</sub>O lines. These lines are predicted in a detailed simulation of the spectrum which calculates 1003 HDO absorption lines with intensities greater than  $2.7 \times 10^{-7}$  cm<sup>-2</sup>/atm with the previously determined dipole-moment parameters. This threshold intensity corresponds to the weakest line observed in the 13 560-14 050 cm<sup>-1</sup> spectral region. These data are available on request from the authors. The total intensities of a- and b-type transitions calculated as a sum of the individual line intensities in the synthetic spectrum were found to be of  $1.4 \times 10^{-2}$  and  $2.4 \times$  $10^{-3}$  cm<sup>-2</sup>/atm, respectively.

A set of 129 accurate energy levels was derived after the spectrum identification by adding the observed transitions to the experimental ground state energy levels of HDO (15). These data together with observed – calculated values, experimental uncertainties of the levels (when observed through several transitions), and number of lines with the same upper level is presented in Table 2. The average accuracy of the energy levels derived through the combination differences of two or more lines was estimated to be 0.007 cm<sup>-1</sup>. In the last column the differences between experimental energy levels and the predictions of Ref. (13) are given. The predicted values of the energy levels are lower by about 0.3 cm<sup>-1</sup> for the lowest rotational levels and by about 2.5 cm<sup>-1</sup> for the highest excited observed levels.

Since HDO represents a light nonrigid molecule undergoing the strong centrifugal distortion effect, the effective Hamiltonian  $H_{vv}$  in the Pade–Borel approximants form (16) was used for the energy level calculations. According to Ref. (16), the matrix elements of the  $H_{vv}$  operator in the  $|jk\rangle$  basis are given by

$$\langle jk | H_{vv} | jk \rangle = E_v + \int_0^\infty \frac{c_0 c_1 + (c_1^2 - c_0 c_2)t}{c_1 - c_2 t} e^{-t} dt$$
$$\langle jk | H_{vv} | jk \pm 2 \rangle = \langle jk | J_{xy}^2 | jk \pm 2 \rangle$$
[1]
$$\times \int_0^\infty \frac{b_0 b_1 + (b_1^2 - b_0 b_2)t}{b_1 - b_2 t} e^{-t} dt$$

		TABLE	E 1			
Wavenumbers,	Intensity, and	Rotational	Assignment	of the $4\nu_3$	Band	of HDO

Observed	Calculated	Predicted	Upper	Lower	Observed	Calculated	Predicted	Upper	Lower
Wavenumber (cm <sup>-1</sup> )	Intensity	Intensity (13)	JK <sub>a</sub> K <sub>c</sub>	J K <sub>a</sub> K <sub>c</sub>	Wavenumber (cm <sup>-1</sup> )	Intensity	Intensity (13)	J K <sub>a</sub> K <sub>c</sub>	J K <sub>a</sub> K <sub>c</sub>
13579.109	1.8E-6	1.2E-06	835	946	13678.430	2.9E-5	1.7E-05	642	743
13589.337	4.0E-6	1.5E-06	762	863	13682.554	2.9E-5	1.8E-05	826	927
13589.337	4.0E-6	1.5E-06	761	862	13685.358	1.4E-5	1.1E-05	422	533
13593.522 b	4.4E-6	1.7E-06	955	1056	13686.478	3.5E-5	2.2E-05	735	836
13593.692	4.4E-6	1.7E-06	954	10 5 5	13686.530	3.5E-5	2.3E-05	734	835
13597.465	6.2E-6	4.2E-06	634	743	13687.519	3.4E-5	2.1E-05	827	928
13602.391	6.1E-6	4.1E-06	633	744	13689.565 a	9.5E-0	2.05.05	512	6 4 2
13604.204	2.9E-6	2.0E-06	12 0	833	13093.003	3,1E-3 3 3E 5	2.0E-05	542	643
13607.106	4.4E-0	1.8E-00	1047	1140	13695.005	J.2E-5	2.0E-05	377	431
13609.702	3.3E-0 4.3E-6	1.3E-00	1046	12 3 10	13696 837	6.7E-6	5 3E-06	414	523
13610.012	4.3E-0 7.3E-6	2.8E-06	854	955	13698 906	1.9E-5	1.5E-05	321	432
13611 149	7.3E-6	3.0E-06	853	954	13699,103	8.7E-6	7.6E-06	716	827
13613 575	2.9E-6	1.3E-06	1138	1239	13701.087	2.1E-6	1.2E-06	836	845
13615.018	9.9E-6	5.9E-06	533	642	13701.464	4.7E-5	3.3E-05	725	826
13616.792	9.7E-6	6.6E-06	532	643	13703.731	5.1E-5	3.5E-05	633	734
13622.278 a	2.1E-6				13704.173 b	5.1E-5	3.4E-05	634	735
13625.430 Б	8.2E-6	3.8E-06	946	1047	13704.760	3.2E-6	2.0E-06	735	744
13625.968	1.7E-6	1.2E-06	616	725	13705.810 b	1.3E-5	1.1E-05	808	919
13627.123	5.5E-6	1.7E-06	12 0 12	13 0 13	13705.976	5.3E-5	3.6E-05	818	919
13627.123	5.5E-6	1.7E-06	12 1 12	13 1 13	13706.053	5.2E-5	3.6E-05	726	827
13627.520	5.7E-6	2.9E-06	11 2 10	12 2 11	13706.172	5.3E-5	3.7E-05	808	909
13628.392	5.8E-6	2.6E-06	11 1 10	12 1 11	13706.338 b	1.3E-5	1.1E-05	818	909
13628.565	1.0E-5	4.7E-06	753	854	13/10.319	3.9E-0	2.8E-06	431	440
13628.565	1.0E-5	4.7E-06	752	855	13/10.480	5./E-5 7.9E 6	4.1E-05	/ J O 9 6 3	817
13629.983	7.0E-6	3.3E-00	1038	10.3.9	12711.459	7.85-6	4.1E-06	863	863
13031.517	1.0E-0	0.8E.06	927	54.2	13713 185	1.6E-5	8 3E-06	762	761
13632.412	5.78-6	4 1E-06	625	734	13713 185	1.6E-5	8.3E-06	761	762
13633 244	6 2E-6	3 1E-06	1037	1138	13713.326	2.5E-5	2.0E-05	221	330
13641 201	7.9E-6	4.0E-06	1028	1129	13713.900	2.5E-5	2.0E-05	220	331
13642.844	2.7E-6	2.2E-06	826	937	13714.379	3.6E-6	1.7E-06	918	937
13643.407	1.4E-5	7.0E-06	845	946	13714.820	3.0E-5	1.6E-05	661	660
13643.954	1.4E-5	7.0E-06	844	945	13714.820	3.0E-5	1.6E-05	660	661
13645.847	1.2E-5	6.0E-06	652	753	13716.135 a	2.5E-6			
13645.847	1.2E-5	6.1E-06	651	752	13717.419	7.0E-6	6.5E-06	726	817
13646.663 a	1.1E-6				13719.022 a	8.1E-6	1 35 07	0.2.5	0.4.4
13647.238	1.9E-6	2.2E-06	1019	11 2 10	13/19.280	7 15 5	1.2E-00	833	844
13647.716	2.5E-6	3.1E-07	11 1 11	12112	13719.020	7.1E-J 3.8E_6	3.3E-03	024	018
13647.710	1.1E-5	7.1E-06	11 0 11	12 0 12	13721.007	6.4E-5	4 7E-05	532	633
13647 787	2 5E-6	3 1E-07	11 1 11	12 0 12	13721.478	6.2E-5	4.0E-05	533	634
13648.121	1.1E-5	5.0E-06	1029	11210	13723.796	1.9E-5	1.8E-05	707	818
13648.495	1.9E-5	1.4E-05	331	440	13723,974	7.5E-5	5.7E-05	625	726
13648.556	1.9E-5	1.4E-05	330	441	13724.150	7.8E-5	5.8E-05	717	818
13649.513	1.3E-5	6.9E-06	937	1038	13724.476	7.8E-5	5.9E-05	707	808
13649.906 b	1.1E-5	5.4E-06	1019	11 1 10	13724.831	1.6E-5	1.3E-05	514	625
13650.775	1.9E-6	2.1E-06	10 2 9	11 1 10	13724.831	1.9E-5	1.7E-05	717	808
13650.919 *	7.9E-7	3.2E-07	10 2 9	11 2 10	13/25.025	5.3E-0	2.9E-06	81/	830
13651.647 b	1.2E-5	6.7E-06	936	103/	13/25.309	1.1E-5 2.7E-6	9.4E-00	313	422
13032.931	4.48-0	3.3E-06	542	551	13727 329 a	3.3E-6			
13656 528	9.7E-6	7.25-06	524	633	13728 999	3.0E-6	1.9E-06	827	836
13662 870	6.9E-6	5.3E-06	624	735	13729.231	8.4E-5	6.8E-05	615	716
13662 960	1 IE-5	5.5E-06	551	652	13730.785	2.7E-6	1.8E-06	818	827
13662.960	1.1E-5	5.5E-06	550	651	13732.143	6.7E-6	3.7E-06	716	735
13663.731	3.5E-6	2.6E-06	515	624	13732.399	1.8E-6	1.1E-06	1029	1028
13665.247	5.2E-6	2.1E-06	872	871	13734.389	3.5E-6	1.9E-06	413	432
13665.247	5.2E-6	2.1E-06	871	872	13734.986	1.8E-6	1.7E-06	735	826
13666.173	3.5E-6	2.8E-06	918	1029	13737.413 b	9.6E-5	8.0E-05	523	624
13666.979	1.1E-5	4.3E-06	771	770	13738.229	6.6E-5	5.2E-05	431	532
13666.979	1.1E-5	4.3E-06	770	771	13738.523	0.6E-5	5.2E-05	432	533
13667.874	1.9E-5	1.4E-05	10 0 10	11011	13/40.930	2.0E-5	2.3E-U3	606	625
13667.874	4./E-6	4.4E-07	10110	11011	13741.288	9.7E-3 1 1E-4	8.0E-03 8.7E-05	524	025
13008.044 8	1.0E-2 2.2E 5	1 3E 05	836	037	13742.000	116-4	89F-05	606	707
13000.343	2.2E-3 2.2E-5	1.3E-05	835	936	13742 955	2.6E-5	2.4E-05	616	707
13672.847	3.2E-6	2.9E-06	928	10 1 9	13746.549	9.0E-6	5.4E-06	707	726
13677.433	1.4E-5	1.1E-05	423	532	13746.875	7.1E-6	5.3E-06	625	634
13678,430 b	2.9E-5	1.7E-05	643	744	13747.184	1.2E-4	1.0E-04	514	615
					1				

*Note.* The calculated (see text) and predicted (13) intensities are given in cm<sup>-2</sup>/atm at 296 K and correspond to pure HDO. The total calculated intensity of the  $4\nu_3$  band is normalized to the total band intensity predicted in Ref. (13). Asterisk denotes the lines belonging to  $5\nu_2 + 2\nu_3$  band. A number of lines marked by "b" are blended by H<sub>2</sub>O lines. In case of unassigned lines (a) and of the lines of the  $5\nu_2 + 2\nu_3$  band (\*), a rough estimation of the experimental intensity is given in the second column instead of the calculated values.

Observed	Calculated	Predicted	Upper	Lower	Observed	Calculated	Predicted	Upper	Lower
Wavenumber (cm <sup>-1</sup> )	Intensity	Intensity(13)	J K <sub>a</sub> K <sub>c</sub>	J K <sub>a</sub> K <sub>c</sub>	Wavenumber (cm <sup>-1</sup> )	Intensity	Intensity (13)	J K <sub>a</sub> K <sub>c</sub>	J K <sub>a</sub> K <sub>c</sub>
13747.766	2.1E-5	1.3E-05	312	423	13798.901	1.4E-4	1.6E-04	211	312
13748.878	1.8E-6	1.2E-06	10 5 5	1056	13799.617 Ь	1.2E-5	1.1E-05	615	624
13749.413	1.7E-5	1.4E-05	212	321	13800,405	1.2E-5	8.4E-06	505	514
13750.004	4.4E-0	2.8E-06	954	955	13802.030	1.0E-5	1.4E-05	513	514
13751.347	9.0E-0	5.7E-00	854	853	13805.720	1.0E-3	1.0E-03	212	313
13752 493	9.0E-6	7.1E-06	524	533	13806.105	1.46-4	1.0E-04	211	220
13753 109	196-5	1 3E-05	753	752	13806 105	1.6E-5	1.4E-05	735	734
13753 109	1.9E-5	1.3E-05	752	753	13807.144 b	1.7E-4	1.9E-04	202	303
13753,406 a	3.1E-6				13807,760	1.9E-5	1.4E-05	312	321
13754.709	3.8E-5	2.5E-05	652	651	13808.038	2.1E-5	2.0E-05	413	422
13754,709	3.8E-5	2.5E-05	651	652	13810.628	2.5E-5	2.5E-05	101	212
13755.046	1.1E-4	1.0E-04	422	523	13810.824	1.8E-5	1.7E-05	625	624
13755.234	4.9E-5	4.1E-05	330	431	13811.380	3.0E-5	2.9E-05	634	633
13755.358	4.9E-5	4.1E-05	331	432	13814.579	5.6E-5	4.9E-05	533	532
13755.864 a	2.3E-6				13814.753 b	1.9E-5	1.8E-05	404	413
13756.161	6.9E-5	4.6E-05	551	550	13815.920	9.7E-5	1.1E-04	110	211
13/30.101	0.9E-3	4.0E-05	550	221	13810.520	9.9E-3	9.9E-05	432	431
13756 555 *	9.0E-0 4.2E.6	7.9E-06	423	432	13817.011	0.7E-5	9.3E-05	431	432
13757 024	3.2E-5	9.9E-06	505	616	13817 790	1.7E-4	1.7E-04	331	330
13758 207	1 1E-4	9.9E-05	423	524	13817.860	1.7E-4	1.7E-04	330	331
13758.660	1.3E-4	1.2E-04	515	616	13817.860	2.2E-5	2.3E-05	414	413
13759.318	1.4E-4	8.2E-05	505	606	13818,190	2.7E-5	2.7E-05	633	634
13760.491	1.2E-5	8.0E-06	606	625	13821.034	9.6E-5	1.1E-04	111	212
13760.953	3.1E-5	2.8E-05	515	606	13821.420	1.3E-5	1.2E-05	734	735
13763.074	4.5E-6	3.4E-06	707	716	13821.540	4.4E-6	2.6E-06	762	661
13763.345	9.6E-6	8.0E-06	422	431	13821.540	4.4E-6	2.6E-06	761	660
13763.435	8.1E-6	5.6E-06	717	716	13822.176	3.1E-5	3.3E-05	524	523
13763.686	9.1E-6	8.5E-06	524	615	13822.598	1.3E-4	1.6E-04	101	202
13764.659 b	1.4E-4	1.4E-04	413	514	13823.823	1.7E-5	1.8E-05	000	111
13771.897	3.6E-5	3.4E-05	404	515	13825.398	2.6E-5	2.6E-05	303	312
13//1.983 0	1.3E-3	5.5E-00	303	324	13827.074	5.3E-0 4.4E-6	3.1E-06	615	630
13773 199	1.1E-4 2.2E-5	2.05-05	110	422	13820.008	4.4E-0 5.6E-5	6.2E-05	423	422
13773 631	9.9E-6	8.0E-05	515	524	13830.694	3.2E-5	3.8E-05	313	312
13774.741	1.1E-4	1.0E-04	322	423	13832.984	1.1E-5	1.1E-05	111	202
13774.974	1.6E-4	1.5E-04	414	515	13834.701	9.7E-5	1,1E-04	3 2 2	321
13775.813 b	1.7E-4	1.6E-04	404	505	13835.300	4.9E-6	2.9E-06	863	762
13777.526	5.6E-6	4.4E-06	827	826	13835.300	4.9E-6	2.9E-06	862	761
13778.886	3.2E-5	3.1E-05	414	505	13836.264	2.3E-5	2.4E-05	101	110
13780.074	4.4E-6	3.3E-06	946	945	13837.091	1.7E-4	2.0E-04	221	220
13780.697	1.3E-5	9.9E-06	404	423	13837.989	1.7E-4	2.0E-04	220	221
13781.310 *	1.6E-4	3.8E-05	312	413	13838.097	7.5E-5	9.4E-05	000	101
13781.843	1.6E-4	1.2E-04	312	413	13838.989	9.2E-5	1.1E-04	321	522
13783.024	1.1E-5 0.4E-6	9.1E-06	010	015	13839.385	5.0E-0	3./E-00	210	211
13785.469	3.6E-5	3.4E-05	303	044 414	13840.500	5.3E=5	4.5E-05	404	321
13786.005	1.9E-5	1.6E-05	744	743	13841 365	5 3E-6	4.0E-06	606	523
13786.474	8.7E-6	7.1E-06	303	322	13841.982	4.8E-5	5.6E-05	422	423
13786.619	8.2E-6	7.9E-06	423	514	13843.805	6.4E-6	2.8E-06	505	422
13787.042	9.0E-6	7.2E-06	844	845	13843.946	3.4E-6	1.9E-06	918	835
13787.237	1.9E-5	1.6E-05	743	744	13844.225	8.8E-7	7.1E-07	1037	1038
13787.847 b	3.8E-5	3.1E-05	643	642	13844.696	4.9E-6	3.1E-06	817	734
13788.177	3.8E-5	3.1E-05	642	643	13845.443	1.0E-6	1.1E-06	515	422
13788.547	1.3E-6	6.0E-07	872	771	13846.662	1.1E-4	1.3E-04	111	110
13788.547	1.3E-6	6.0E-07	871	770	13847.329	2.5E-5	2.8E-05	523	524
13789.340	7.0E-5	5.8E-05	542	541	13847.889	1.2E-5	9.0E-06	652	551
13/89.400	7.UE-3	5.8E-05	541	542	1384/.889	1.2E-3	9.0E-06	021	33U 840
13789.38/	3.4E-0 7.9E-5	2.9E-00 8 0E 05	202	221	13848.997	3.9E-0 3.8E-6	2.3E-00 2.3E-06	904	860 860
13707.077	) .912-5 ] 2F-4	1.0E-03	441	521 440	13852 325	1 0F-4	1 3F-04	110	111
13790 599	1.2E-4	1 0E-04	440	440	13854 885	1.2E-5	1.4E-05	624	625
13790.770	1.7E-4	1.7E-04	313	414	13857.231	4.8E-5	6.2E-05	211	212
13791.010	7.8E-5	7.9E-05	221	322	13861.933 b	1.4E-5	1.1E-05	753	652
13791.678	1.8E-4	1.9E-04	303	404	13861.933	1.4E-5	1.1E-05	752	651
13795.886	9.9E-6	8.9E-06	726	725	13862.592	2.5E-6	1.5E-06	1065	964
13796.992	3.0E-5	2.9E-05	313	404	13862.657	2.5E-6	1.5E-06	1064	963
13797.873	7.5E-6	6.6E-06	836	835	13862.891 a	2.4E-6		_	
13798.126	3.1E-5	3.1E-05	202	313	13863.910 *	2.7E-5	8.1E-06	312	313
					t				

TABLE 1—Continued

Observed Wavenumber (cm <sup>-1</sup> )	Calculated Intensity	Predicted Intensity (13)	Upper J K. K.	Lower JK, K.	Observed Wavenumber (cm <sup>-1</sup> )	Calculated Intensity	Predicted Intensity (13)	Upper J K. K.	Lower J K. K.
13864 132	6.1E-6	6.4E-06	725	726	13904,599	4.5E-6	3.6E-06	716	717
13864 441	2.7E-5	2.7E-05	312	313	13904.802	4.9E-6	3.8E-06	10 5 5	954
13866.111	9.7E-7	1.2E-06	624	533	13905.784	7.7E-6	8.5E-06	625	616
13867.268	2.7E-5	2.6E-05	542	441	13905.893	6.0E-6	6.4E-06	716	707
13867.268	2.7E-5	2.6E-05	541	440	13906.415	1.8E-4	2.6E-04	404	303
13868.774	7.5E-5	1.0E-04	101	000	13907.400	6.5E-5	7.5E-05	634	533
13869.199 b	3.0E-5	3.4E-05	211	202	13907.782	2.9E-7	2.4E-07	12 2 10	12111
13873.510	2.9E-5	2.5E-05	312	303	13908.081	4.9E-6	3.7E-06	625	606
13873.510	1.6E-5	2.0E-05	413	414	13908.787 *	3.8E-6	1.1E-06	515	414
13874.600	3.8E-6	3.4E-06	936	927	13909.155	1.2E-4	1.5E-04	524	423
13875.155	1.9E-6	1.7E-06	10 3 7	1028	13909.663	2.3E-5	2.2E-05	845	744
13875.606	6.4E-6	6.2E-06	835	826	13910.896	1.8E-4	2.4E-04	515	414
13875.757 b	2.3E-5	2.5E-05	523	514	13911.306 b	6.1E-5	7.2E-05	633	532
13875.920	1.2E-5	8.2E-06	854	753	13911.968 b	2.2E-5	2.1E-05	844	743
13876.042	2.6E-5	2.9E-05	422	413	13912.850	4.0E-6	2.6E-06	726	707
13876.042	1.2E-5	9.0E-06	853	752	13913.410	1.4E-4	2.1E-04	413	312
13877.915	2.2E-5	2.5E-05	321	312	13913.891	1.4E-5	2.0E-05	221	110
13878.188	9.3E-6	9.4E-06	734	725	13915.464	1.8E-4	1.3E-04	505	404
13878.442	7.1E-7	6.2E-07	661	652	13917.119	1.3E-5	1.7E-05	220	111
13878.442	7.1E-7	6.1E-07	660	651	13917.119	1.3E-5	1.9E-05	515	404
13879.163	1.4E-5	1.7E-05	111	000	13917.400	3.1E-6	3.3E-06	827	818
13879.163	5.1E-5	5.7E-05	432	331	13919,120	1.1E-4	1.4E-04	523	422
13879.567	5.1E-5	5.7E-05	431	330	13919.498	9.2E-6	1.4E-05	606	515
13879.695	2.2E-5	2.6E-05	413	404	13920.289	1.6E-4	2.1E-04	616	515
13880.628	1.1E-5	1.1E-05	725	716	13920.583	5.3E-5	6.0E-05	735	634
13880.753 b	1.3E-5	1.5E-05	220	211	13920.748 b	1.0E-4	1.3E-04	625	524
13881.138	1.1E-6	9.4E-07	954	945	13922.157 a	8.0E-7			
13881.532	3.4E-5	3.2E-05	643	542	13923.170	1.6E-5	1.4E-05	946	845
13881.792 b	3.4E-5	3.2E-05	042	541	13923.414	1.6E-4	2.1E-04	60.6	505
13882.975	1.3E-4	1.9E-04	202	101	13923.755	1.3E-0	3.5E-07	555	514
13885.729	1.3E-3	1.7E-03	203	212	13924,181	9.16-0	1.42-05	010	202
13003.123	6 DE 6	9.9E-03	926	220	13923.393	1.2E-3	1.7E-03	522	211
13885.033	0.2E-0	1.4E-05	532	573	13920.729	1.3E-4	175.04	514 717	413
13887 762	1.5E-5	1.46-05	514	505	13920.737	1.50-4	1.72-04	1258	1157
13888 586 h	1.0E-5 4.5E-6	1.7E-05	743	734	13030.209	1.42-0	1.02-00	707	60.6
13889 022	1.6E-4	2 16-04	313	212	13931 149	8 2E-5	1.0E-04	707	625
13889 787	8 3E-6	6 1E-06	955	854	13932 765 h	3.8E-5	4 3E-05	836	735
13890 258	8 3E-6	6 2E-06	954	853	13935 378	9 1E-6	1.4E-05	423	312
13890 811	1.1E-5	1.3E-05	431	422	13936.347 b	1.0E-4	1.12E-04	81.8	717
13890.980	1.7E-5	2.2E-05	212	101	13937.473 b	9.9E-5	1.2E-04	80.8	707
13891,395	1.3E-5	1.5E-05	322	313	13940.177	6.0E-5	7.3E-05	827	726
13891.582	3.1E-6	2.9E-06	927	918	13941.555	1.4E-5	2.0E-05	331	220
13891.873	1.8E-6	1.8E-06	551	542	13943.197	6.4E-6	1.0E-05	524	413
13891.873	1.8E-6	1.8E-06	550	541	13943.702	7.0E-5	7.5E-05	909	808
13892.397	5.5E-6	5.6E-06	642	633	13943.702	2.5E-5	2.7E-05	937	836
13892.696	4.2E-6	4.2E-06	744	735	13946.199	7.8E-6	7.6E-06	1046	945
13893.516	6.7E-5	6.9E-05	533	432	13946.536	8.2E-5	1.1E-04	716	615
13893.844	7.7E-6	8.8E-06	330	321	13946.717	3.2E-5	3.8E-05	835	734
13894.266 b	5.3E-6	5.4E-06	643	634	13947.953	4.0E-5	4.5E-05	928	827
13895.002	6.6E-5	7.6E-05	532	431	13948.103 a	7.0E-6			
13895.165	1.0E-5	1.2E-05	432	423	13949.071	4.7E-5	1.4E-05	10 1 10	919
13895.367	1.0E-5	1.0E-05	533	524	13949.338	1.7E-5			
13895.457	7.4E-6	8.5E-06	331	322	13949.430	4.7E-5	1.7E-05	10 0 10	909
13895.457	1.3E-5	1.5E-05	423	414	13949.690 a	2.3E-5			
13895.674	1.7E-4	2.4E-04	303	202	13950,980	6.5E-5	8.9E-05	725	624
13895.674	3.1E-5	2.9E-05	744	643	13952.712	5.7E-5	7.5E-05	817	716
13895.901	5.5E-6	5.8E-06	542	533	13953.110	1.4E-5	1.5E-05	10.3.8	937
13896.189	8.4E-0	9.0E-06	634	025	13933,488	2.5E-0	4.5E-06	/26	615
13890,430	1.1E-4 3.0E 5	1.3E-04	423	542	13934.141 D 13054 240 L	2.35-3	2.7E-05	1029	928
13090.374	5.0E-5	2.96-03	143	6042	13754.348 0	2.7E-J	1.10-00	11 1 11	10 1 10
13070.041	7.75-0 1.4E-4	4.85-05	313	211	13956 600	1 36-6	2.10-05 2.6E-06	227	714
13898 632	1.4E-4	1.5E-04	312	211	13956 943 *	1.5E-6	1.4E-06	1029	0 1 0
13900 435	1 8F-4	2 5E-04	414	313	13957 175	3 8E-5	4 6F-05	Q 1 8	817
13900 960	1.7E-5	2.4E-05	313	202	13959 000	1.7E-5	1.6E-05	12 1 12	1111
13901.942	1.0E-4	1.4E-04	422	321	13959.078	1.7E-5	L6E-05	12 0 12	11011
13902.200	2.2E-6	2.2E-06	937	928	13959.491	1.4E-5	1.4E-05	11 2 10	10.2 9
13903.551	5.1E-6	3.8E-06	1056	955	13959.882	9.7E-6	1.4E-05	441	330
13904.233	5.3E-6	4.4E-06	524	505	13959.882	9.7E-6	1.4E-05	440	331
		-	-		=			•	

**TABLE 1**—Continued

Observed	Calculated	Predicted	Upper	Lower	Observed	Calculated	Predicted	Upper	Lower
Wavenumber (cm <sup>-1</sup> )	Intensity	Intensity (13)	J K <sub>a</sub> K <sub>c</sub>	J K <sub>a</sub> K <sub>c</sub>	Wavenumber (cm <sup>-1</sup> )	Intensity	Intensity (13)	J Ka Kc	J K <sub>a</sub> K <sub>c</sub>
13960.626	2.3E-5	2.8E-05	1019	918	13983.839	2.2E-6			
13961.012	8.1E-6	8.3E-06	1139	1038	13984.568	1.4E-6	2.5E-06	523	4   4
13962.947	9.2E-6	8.3E-06	13 0 13	12 0 12	13984.568	1.6E-6	3.0E-06	735	624
13963.352	1.4E-5	1.3E-05	11 1 10	1019	13984.965	7.5E-6	9.0E-06	1129	1028
13963.761	7.9E-6	7.7E-06	12 2 11	11 2 10	13985.159	1.2E-6	1.4E-06	762	651
13964.079	4.3E-5	5.8E-05	826	725	13985.159	1.2E-6	1.4E-06	76 l	652
13964.438	1.9E-5	2.4E-05	936	835	13985.458 a	1.0E-6			
13965.695	8.3E-7	8.0E-07	771	660	13985.626	1.8E-6	1.8E-06	13 2 11	1220
13965.695	8.3E-7	8.0E-07	770	661	13985.753 a	1.1E-6			
13966.105	7.8E-6	7.6E-06	12111	11 1 10	13986.098	3.8E-6	4.1E-06	12 2 10	1129
13966.214	4.7E-6	9.4E-07	14 0 14	13 0 13	13987.374	3.1E-6	5.1E-06	643	532
13967.146	5.6E-6	7.9E-06	533	422	13987.722 a	1.0E-6			
13967.146	4.0E-6	3.7E-06	13 2 12	12 2 11	13988.188 a	6.9E-7			
13967.701	6.7E-6	9.6E-06	422	303	13988.388	3.0E-6	5.0E-06	642	533
13968.480	4.0E-6	3.7E-06	13 1 12	12 1 11	13990.024 a	9.8E-7			
13968.784	2.2E-6	2.9E-07	15015	14 0 14	13992.219	2.9E-7	6.7E-07	937	826
13968,784	2.2E-6	2.9E-07	15 1 15	14 1 14	13994.128	5.5E-6	6.4E-06	1138	1037
13968.918 a	1.8E-6				13996.179	2.2E-6	2.0E-06	431	312
13969.786	5.2E-6	6.9E-06	551	440	13997.228	1.4E-6	2.2E-06	752	643
13969.786	5.2E-6	6.9E-06	550	441	13998.409	5.5E-7	6.9E-07	863	752
13970.709	1.0E-6	6.7E-07	16 0 16	15015	13998.409	5.5E-7	6.9E-07	862	753
13970.709	1.0E-6	6.7E-07	16116	15 1 15	14003.031	1.4E-6	2.5E-06	743	634
13971.641	2.3E-6	2.7E-06	661	550	14004.165	2.6E-6	2.9E-06	1239	1138
13971.641	2.3E-6	2.7E-06	660	551	14004.897 a	6.6E-7			
13971.907 a	2.6E-6				14007.680	4.0E-6	4.2E-06	532	413
13973.619	4.8E-6	7.9E-06	532	423	14008.319 a	1.7E-6			
13973.879	5.7E-6	8.7E-06	542	431	14010.157	1.1E-6	1.1E-06	13310	1239
13974.195	2.6E-5	3.3E-05	927	826	14010.292	6.2E-7	8.9E-07	854	743
13976.905 a	1.9E-6				14010.704	6.2E-7	1.0E-06	853	744
13977.053	3.0E-6	5.4E-06	634	523	14011.820	1.4E-6	9.9E-07	432	313
13981.242	1.4E-5	1.8E-05	1028	927	14018.335 a	7.4E-6			
13981.472 a	8.8E-7				14018.978 a	3.6E-6			
13981.722 a	1.0E-6				14020.460	5.7E-6	6.5E-06	633	514
13983.604	2.9E-6	4.0E-06	652	541	14026.414 a	7.7E-7			
13983.604	2.9E-6	4.1E-06	651	542	14032.620	1.9E-6	1.2E-06	533	414

with

$$c_{0} = \left[A - \frac{B+C}{2}\right]k^{2} + \frac{B+C}{2}j(j+1)$$

$$c_{1} = -\Delta_{k}k^{4} - \Delta_{jk}k^{2}j(j+1) - \Delta_{j}j^{2}(j+1)^{2}$$

$$2c_{2} = H_{k}k^{6} + H_{kj}k^{4}j(j+1) + H_{jk}k^{2}j^{2}(j+1)^{2}$$

$$+ H_{j}j^{3}(j+1)^{3} + L_{k}k^{8} + \cdots$$

$$B - C$$
[2]

$$b_{0} = \frac{1}{2}$$

$$b_{1} = -\delta_{k}[k^{2} + (k \pm 2)^{2}] - 2\delta_{j}j(j + 1)$$

$$2b_{2} = h_{k}[k^{4} + (k \pm 2)^{4}] + h_{jk}[k^{2} + (k \pm 2)^{2}]$$

$$\times j(j + 1) + 2h_{j}j^{2}(j + 1)^{2} + \cdots$$
[3]

The integrals in Eqs. [1] can be estimated in the following way

$$\langle jk | H_{vv} | jk \rangle = E_v + (c_0 c_2 - c_1^2)/c_2 + c_1 Ei(c_1/c_2) \\ \times (c_1/c_2)^2 \exp(-c_1/c_2),$$
 [4]

where  $Ei(-x) = -\int_x^{\infty} e^{-t} t^{-1} dt$  is the exponential integral.

The  $\langle jk | H_{vv} | jk \pm 2 \rangle$  matrix elements are evaluated similarly by replacing  $c_n$  by  $b_n$ . It should be stressed that the rotational and centrifugal distortion constants in Eqs. [2] and [3] have their usual meaning accepted in the literature.

The final rms achieved in the fitting of 121 energy levels with 13 varied parameters is 0.012 cm<sup>-1</sup>, that is close to the average accuracy of the experimental data. The set of rotational and centrifugal distortion constants for the (004) vibrational state of HDO together with 68% confidential intervals is presented in Table 3. The nonvaried sextic parameters were fixed to the corresponding values of the (002) state derived from a large set of rovibrational energy levels in (6), since the vibrational dependence of these parameters is rather weak for the states with the same  $V_2$  quantum number.

Figure 1 shows a comparison of the ICLAS spectrum near the  $4\nu_3$  band center with the simulated spectrum obtained with the rovibrational parameters listed in Table 3 and the predictions of Partridge and Schwenke.

The vibrational dependence of the rotational *A*, *B*, and *C* constants of HDO on the stretching  $V_3$  quantum number is presented on Fig. 2 up to  $V_3 = 5$ . The observed linear dependence leads to the determination of the  $\alpha^3$  constants:  $\alpha_A^3 = -0.9933(78)$ ,  $\alpha_B^3 = -0.01169(13)$ , and  $\alpha_C^2 = -0.07889(10)$  cm<sup>-1</sup>.

TABLE 2Rotational Energy Levels (cm<sup>-1</sup>) of the (004) Vibrational State of HD<sup>16</sup>O

JK.K.	Eabe	0 - C	σ	N	Δ	JK <sub>a</sub> K <sub>c</sub>	Eobs	0 - C	σ	N	Δ
000	13853 631	0.001		1	-0.30	818	14340,767	0.003		1	-0.96
101	13868 765	-0.012	0.008	4	-0.31	817	14426.644	-0.012	0.011	3	-0.60
111	13879 159	0.003	0.002	4	-0.31	82.7	14430.610	0.021	0.006	5	-0.59
110	13882 121	0.005	0.012	3	-0.30	82.6	14484.207	0.016	0.007	4	-0.95
20.2	13898 504	-0.010	0.015	3	-0.31	836	14509.662	-0.007	0.009	3	-0.91
202	13906 486	0.005	0.007	4	-0.30	83.5	14528.686	0.001	0.007	5	-0.58
212	13015 359	0.005	0.002	2	-0.31	845	14592 985	0.002	0.001	2	-0.55
221	13946 387	0.000	0.002	3	-0.30	844	14595 597	0.010	0.008	2	-0.87
221	13046.007	-0.005	0.005	3	-0.30	854	14693 917	0.022	0.013	4	-0.92
220	13940.922	-0.000	0.005	5	-0.30	853	14694 039	-0.001	0.012	3	-0.53
212	12047 147	0.000	0.000	6	-0.30	863	14816 425	-0.011	0.003	2	-0.76
212	13947.147	0.004	0.007	5	0.35	860	14816 421	-0.011	0.005	2	-0.70
212	13904.027	0.027	0.008	5	-0.33	872	14060 081	0.002	0.000	ź	-0.74
322	13991,778	0.004	0.007	5	-0.30	871	14960.081	0.002	0.002	2	-0.74
321	13994.300	0.002	0.008	5	-0.51	000	14/56 217	0.002	0.002	1	1 1 2
331	14050.850	0.004	0.010	3	-0.29	909	14450.217	0.003		1	-1.12
330	14050.897	0.001	0.013	4	-0.29	919	14450.205	-0.003	0.004	1	-1.12
404	13997.750	-0.003	0.009	4	-0.37	918	14557 002*	0.021	0.004	7	-0.93
4 1 4	14000.832	0.001	0.004	4	-0.38	928	14557,905	0.093	0.004	2	-0.94
413	14029.868	-0.013	0.010	4	-0.32	927	14027.303	-0.105	0.014	2	-1.10
423	14051.843	0.010	0.005	8	-0.30	937	14043.304	-0.013	0.005	2	-1.07
422	14059.027	0.010	0.006	0	-0.37	930	140/0.230	-0.009	0,003	2	-0.92
432	14112.199	-0.008	0.010	2	-0.36	946	14/31./21	0.004	0.012	2	-0.87
431	14112.646	0.001	0.005	0	-0.29	945	14/3/.834	0.011	0.001	1	-1.02
441	14192.932	0.010	0.002	2	-0.25	955	14832.317	0.002	0.001	2	-0.96
440	14192.917	-0.011	0.011	2	-0.34	954	14832.781	-0.014	0.006	3	-0.83
505	14065.638	0.004	0.003	4	-0.38	964	14954.000	0.016		1	-0.74
515	14067.272	0.025	0.005	7	-0.41	963	14954.001	-0.002		1	-0.87
514	14109.706	-0.011	0.008	5	-0.33	10010	14583.858	0.011		1	-1.11
524	14126.179	-0.004	0.013	8	-0.33	10 1 10	14583,861	-0.018		1	-1.48
523	14140.957	-0.011	0.006	3	-0.43	10 1 9	14696.361	0.030	0.001	2	-1.02
533	14188.994	-0.010	0.008	8	-0.40	10 2 9	14697.248*	-0.141	0.002	3	-1.03
532	14190.673	-0.004	0.008	7	-0.36	1028	14782.889	-0.034	0.004	2	-1.07
542	14269.574	-0.001	0.017	6	-0.33	1038	14794.485*	-0.040	0.008	2	-1.06
541	14269.639	0.009	0.004	2	-0.36	1037	14840.002	-0.005	0.003	2	-1.05
551	14372.122	0.005	0.006	4	-0.43	1047	14885.544*	0.040		1	-0.99
550	14372.126	0.008	0.006	4	-0.29	1046	14897.843	0.021	0.008	2	-1.02
606	14145.365	0.003	0.006	5	-0.54	1056	14986.336	-0.014		1	-1.76
616	14146.120	-0.028	0.010	4	-0.60	1055	14987.680	-0.011	0.008	2	-0.96
615	14203.154	-0.005	0.005	3	-0.40	1065	15107.029	0.006		1	-0.88
625	14214.396	0.009	0.005	4	-0.40	1064	15107.096	0.001		1	-1.76
624	14239.765	0.002	0.010	4	-0.59	11011	14723.486	0.001	0.016	2	-2.14
634	14281.059	-0.004	0.012	5	-0.57	11111	14723.490	-0.010	0.012	2	-2.09
633	14285.702	0.004	0.008	4	-0.38	11 1 10	14848.418*	-0.196	0.002	2	-1.08
643	14361.779	-0.015	0.005	2	-0.38	11 2 10	14849.062*	-0.072	0.005	2	-1.02
642	14362.060	0.001	0.006	3	-0.53	1129	14949.815	-0.017		1	-2.01
652	14463.862	0.005	0.009	4	-0.49	1139	14956.813	0.012	0.008	2	-1.98
651	14463.860	-0.003	0.010	4	-0.33	1138	15018.698	-0.002	0.002	2	-1.04
661	14587.609	-0.001	0.001	3	-0.41	12 0 12	14875.096	-0.008	0.010	2	-2.09
660	14587.610	0.001	0.001	3	-0.44	12 1 12	14875.117	0.006	0.006	2	-2.08
707	14236.989	-0.003	0.008	5	-0.61	12 1 11	15012.579*	-0.089		1	-1.04
717	14237.354	-0.005	0.002	3	-0.59	12211	15012.885	-0.032		1	-1.03
716	14309.048	-0.010	0.003	7	-0.54	12 2 10	15127.800	0.012	0.011	2	-1.95
726	14315.999	0.003	0.010	6	-0.54	1239	15210.919	0.002		1	-1.79
725	14354.552	0.008	0.005	4	-0.62	1258	15340.775	-0.004		l	-1.86
735	14388.088	0.001	0.010	4	-0.60	13 0 13	15038.661	-0.014		1	-2.09
734	14398.320	-0.007	0.006	3	-0.53	13 1 12	15188.509	-0.025		1	-1.95
744	14469,607	-0.008	0.007	2	-0.54	13 2 12	15188.682	0.031		1	-1.91
743	14470.549	0.002	0.007	4	-0.87	13 2 11	15316.843	0.009		1	-1.98
753	14571.109	0.017	0.013	2	-0.81	13 3 10	15415.282	-0.003		1	-1.89
752	14571.120	-0.007	0.005	3	-0.50	14 0 14	15214.178	0.015		1	-1.99
762	14694.327	-0.001	0.010	4	-0.45	15015	15401.530	-0.001		1	-2.58
761	14694.327	-0.002	0.010	4	-0.75	15115	15401.542	0.011		1	-2.69
771	14838.498	-0.001	0.012	2	-0.65	16016	15600.732	-0.007		1	-2.54
770	14838.498	-0.001	0.012	2	-0.38	16116	15600.737	-0.002		1	-2.54
80.8	14340.600	0.002		1	-0.96						

Note. Asterisks denote the energy levels excluded from the fitting. o - c are observed minus computed energy levels values.  $\sigma$  denotes the experimental uncertainties of the levels given in cm<sup>-1</sup>. N is the number of lines sharing the same upper level.  $\Delta$  is the difference between the experimental energy levels and the predictions of Ref. (13) (in cm<sup>-1</sup>).

E	13853.63111(390)	δ <sub>j</sub>	1.5062(110)×10 <sup>-4</sup>
A	19.44264(100)	H <sub>k</sub>	3.355(110)×10 <sup>-5</sup>
В	9.057657(240)	$H_{kj}$	-9.585(490)×10 <sup>-6</sup>
С	6.090345(190)	H <sub>jk</sub>	2.301(100)×10 <sup>-6</sup>
$\Delta_{\mathbf{k}}$	9.1429(560)×10 <sup>-3</sup>	Hj	4.6×10 <sup>-8</sup>
$\Delta_{jk}$	2.980(200) ×10 <sup>-4</sup>	h <sub>k</sub>	1.3×10 <sup>-5</sup>
$\Delta_{j}$	4.18087(460) ×10 <sup>-4</sup>	$\mathbf{h}_{\mathbf{kj}}$	1.1×10 <sup>-6</sup>
$\delta_k$	1.63888(680) ×10 <sup>-3</sup>	h <sub>j</sub>	2.004(340)×10 <sup>-8</sup>

 TABLE 3

 Rotational and Centrifugal Distortion Constants of the (004) Vibrational State of HD<sup>16</sup>O (in cm<sup>-1</sup>)

It was found in the process of the fitting that the (004) HDO vibrational state may, in fact, be considered as isolated within the experimental accuracy up to  $J \le 8$ . The positions of some of the energy levels with rotational quantum number J > 8 seem to be perturbed up to  $0.2 \text{ cm}^{-1}$ . In addition, some slight perturbations of the lower *J* energy levels due to the (052) state were also detected: [312], [515], [616] calculated levels deviate significantly from the experimental ones (by at least twice the rms deviation of the fitting). The eight perturbed energy levels deviate from the calculation by a value exceeding 0.04 cm<sup>-1</sup> are marked by an asterisk in Table 2 and were excluded from the fitting.

To localize the resonant perturber, the accurate HDO rovibrational energy level predictions from Ref. (13) were used together with our own estimations. The most probable candidate for the perturber was the (052) vibrational state at 13 797.53 cm<sup>-1</sup>. This highly excited bending state is 56 cm<sup>-1</sup> lower in energy than the (004) state but, due to the large value of the rotational constant  $A \sim 60$  cm<sup>-1</sup>, the rotational levels are already tuned to a close resonance for the  $K_a = 1$  levels. We found that at least six of the eight perturbed levels of the (004) state excluded from the fit fall into close resonance with a rotational levels of the (052) state. Such interactions have a local character since the energy levels are in resonance only for small  $K_a$  values as a consequence of the quicker increase in the energy of the (052) rotational sublevels with  $K_a$ . Such unusual

resonance, as compared with conventional types of resonance interaction, was first found for the (220) and (070) vibrational states of  $H_2O(17)$ , leading to the observation of several energy levels of the (070) state.

In confirmation of our analysis, Ref. (13) predictions clearly showed the vicinity of the most part of (004) perturbed energy levels with the corresponding (052) values. It should, however, be noted that the vibrational assignments of Ref. (13) are often ambiguous due to strong mixing of the rovibrational wavefunctions: the same set of vibrational and rotational quantum numbers is attached to different energy level values. Reference (13) gives two energy levels with close, though different, numerical values both for the [312] and [515] (004) states. Additional calculations involving the (052) state low-lying energy levels were required to prove that, in fact, one of the nearly degenerate levels belonged to the (052) state, though Ref. (13), gives different energy values for these levels.

Finally, seven transitions involving the energy levels of the (052) state were found in the spectrum borrowing their intensities through resonance coupling with rather strong  $4\nu_3$  perturbed lines. These  $5\nu_2 + 2\nu_3$  transitions are given in Table 4 together with their resonance partners. Table 4 shows that all the  $5\nu_2 + 2\nu_3$  lines correspond to the strongest transitions of the  $4\nu_3$  band line-partners with a clear proportionality in the intensity values of both sets. Numerical predictions (13) for  $5\nu_2 + 2\nu_3$  line intensities and upper state levels are also given



FIG. 1. Comparison of (a) the ICLAS spectrum recorded with an equivalent path length of 15 km and a total vapor pressure of 20 Torr with (b) the stick spectrum calculated with the parameters of Table 4 and with the predictions of Partridge and Schwenke (c). The simulated spectrum was obtained with  $1.3 \times 10^{-2}$  and  $2.2 \times 10^{-3}$  cm<sup>-2</sup>/atm total intensity for the A- and B-type transitions, respectively. Asterisks mark the H<sub>2</sub>O lines [Ref. (*11*)]. Note the shift of the Ref. (*13*) predictions to the higher wavenumbers.

for comparison in this table. In spite of the high bending excitation of the (052) level, the calculated line intensities agree satisfactorily with the experimental measurements, except for the [515] energy level. Indeed, Partridge and Schwenke predict that the strongest lines reaching the [515] (052) energy level should originate from [404] and [606] ground state levels while we observe this level through other lines arising from the [414] and [616] rotational levels. As a proof of the correctness of our analysis, the observed deviation of the three (004) levels from their unperturbed position agree with their relative position compared to the interacting rotational levels of the (052) state (see Table 4): a positive shift is observed both for [312] and [515] while the shift is negative for the [10 2 9] level.

We did not make any attempt to take into account the resonance interaction between (004) and (052) states in the fitting process, since the resonance perturbations were small enough and had a local character, not hindering the reasonable assignment of the perturbed lines.

In conclusion of this section, it is worth comparing our results with those obtained recently in Ref. (3). Our energy

levels agree within 0.13 cm<sup>-1</sup> and we have confirmed all of the 60 assignments of Ref. (3). As to the spectroscopic constants, it seems that there are misprints in Table III of Ref. (3): the values of  $\Delta_k$ ,  $\Delta_{jk}$ ,  $\Delta_j$ ,  $\delta_k$ ,  $\delta_j$  constants should be multiplied by a factor of  $10^{-2}$ . It comes as no surprise that the parameters of Ref. (3) derived from the limited set of transitions are not accurate enough to predict properly the energy levels with high values of J and  $K_a$ .

We have estimated, using our total *a*- and *b*-type transition intensities, the angle between the transition dipole moment and the OH bond for  $4\nu_3$  using the formula (5) of Ref. (3) and have obtained a value of 36.7°, which is very close to the result in the Ref. (3) result (38°). We have also estimated the angle for  $2\nu_{OH}$  to be 23° from the data in Refs. (5, 6).

## 4. CONCLUSIONS

The overtone spectrum of the HDO molecule in the 13 560– $14050 \text{ cm}^{-1}$  spectral region was recorded by ICLAS and theoretically treated yielding 406 rovibrational lines assignments and 129 accurate rotational sublevels of the high over-



**FIG. 2.** Vibrational dependence of the *A*, *B*, and *C* rotational constants with  $V_3$  quantum number. The differences between the *A*, *B*, *C* constants of the ground state and those of the  $nV_3$  (n = 1-5) excited states are plotted. Note that for convenience,  $\Delta B$  and  $\Delta C$  were multiplied by a factor of 10. The rovibrational constants  $\alpha_A^3$ ,  $\alpha_B^3$ ,  $\alpha_B^$ 

tone (004) state. The (004) vibrational state was found to be nearly isolated. The precise set of the spectroscopic parameters of the effective rotational Hamiltonian in the Pade–Borel form was derived from the fitting of the energy levels providing an rms deviation of 0.012 cm<sup>-1</sup>. A detailed synthetic spectrum of the HDO absorption was calculated in the analyzed region corresponding to more than 906 line positions and relative intensities.

The weak local resonance interaction between the (004) state and the highly excited bending (052) state was found to take

TABLE 4Transitions of the  $5\nu_2 + 2\nu_3$  Band Borrowing Their Intensities from the Strong Line Partners of the  $4\nu_3$  Band

			((	)04)	1.1977ara					
Upper J K <sub>a</sub> K <sub>c</sub>	Lower J K <sub>a</sub> K <sub>c</sub>	Observed Wavenumber	Calculated Intensity cm <sup>-2</sup> /atm	Predicted Intensity (13)	Upper Energy Level	Observed Wavenumber	Observed Intensity cm <sup>-2</sup> /atm	Predicted Intensity(13)	Upper Energy Level	Predicted Energy (13)
312	211	13898.632	1.4E-04 2.9E-05	1.5E-04 2.5E-05	13964.817 13964.840	13898.104	1.3E-05	4.8E-05 7.6E-06	13964.288	
312	313	13864.441	2.7E-05	2.7E-05	13964.832 13964.825	13863.910	5.6E-06	8.1E-06 4.2E-06	13964.301	13964.88
312	413	13781.843	1.6E-04 2.1E-05	1.2E-04 1.3E-05	13964.827	13781.310	1. 3E-05	3.8E-05 4.3E-06	13964.294	
515 515 515 515	404 414 514	13917.119 13910.896 13802.030	1.3E-05 1.8E-04 1.6E-05	1.9E-05 2.3E-04 1.4E-05	14067.275 14067.278 14067.267	13908.787	3.8E-06	1.1E-04 1.1E-06 2.9E-06 5.5E-06	14065.169	14066 02
515 515 515 515	5 2 4 6 0 6 6 1 6 6 2 4	13773.631 13760.953 13758.660 13663.731	9.9E-08 3.1E-05 1.3E-04 3.5E-06	2.8E-05 1.2E-04 2.6E-06	14067.268 14067.268 14067.275 14067.280	13756.555	4.2E-06	4.4E-05 2.3E-05	14065.171	14000.02
1029 1029 1029	928 1028 11110	13954.141 13732.399 13650.775	2.5E-05 1.8E-06 1.9E-06	2.7E-05 1.1E-06 2.1E-06	14697.238 14697.249 14697.249	13956.943	1.6E-06	1.5E-06 - - 3.2E-07	14700.040	14701.23

place yielding to seven observed transitions of the  $5\nu_2 + 2\nu_3$  band.

The wide comparison of the presented energy level data with recent accurate *ab initio* calculations by Partridge and Schwenke has shown their agreement to within 2.7 cm<sup>-1</sup>. The new information obtained in this work will allow a further refinement of the  $H_2O$  molecule isotopically invariant potential energy surface.

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