High-Order Resonance Interactions in HDO: Analysis of the Absorption Spectrum in the 14 980–15 350 cm⁻¹ Spectral Region

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The absorption spectrum of the HDO molecule recorded by intracavity laser absorption spectroscopy in the 14 980–15 350 cm⁻¹ spectral region was assigned and modeled in the frame of the effective Hamiltonian approach. The spectrum (496 lines) results, mainly, from transitions to the rotational sublevels of the (014) bright state. An important number of transitions involving the (142) and (0 12 0) highly excited bending states could be identified, borrowing their intensities through high-order resonance interactions with the (014) state. An original feature shown by the present analysis is that all the transitions involving unperturbed energy levels of the (014) state are exclusively of *A* type, while both *A*- and *B*-type transitions are observed when the upper states are perturbed by the resonance interactions. One hundred forty-five energy levels of the three interacting states were derived from the spectrum and fitted to the effective rotational Hamiltonian in Pade–Borel approximants form with 29 varied parameters yielding an rms deviation of 0.038 cm⁻¹. A few energy levels are affected by additional local resonances with perturbers which have been identified. Finally, 48 transitions of the very weak $6\nu_1$ band were assigned and fitted as an isolated band. @ 2000 Academic Press

1. INTRODUCTION

This paper is a part of our study of the HDO near-infrared and visible rovibrational spectrum started in Ref. (1). The intracavity laser absorption spectroscopy (ICLAS) technique was used to record the HDO overtone spectrum between 13 160 and 17 100 cm⁻¹. The part of the ICLAS spectrum between 13 560 and 14 050 cm⁻¹ dominated by the $4\nu_3$ band transitions was analyzed in Ref. (1) leading to the detailed knowledge of the (004) state rotational energy levels structure. (Note that, contrary to the recommendations of IUPAC, we use the traditional labeling of the stretching vibration with ν_1 and ν_3 standing for the OD and OH stretching, respectively.) In the present report, we limited our analysis to the 14 980-15 350 cm⁻¹ spectral region which corresponds to rovibrational transitions involving the (014) upper vibrational state. The upper energy region between 15 500 and 17 100 cm⁻¹ includes the stronger (005) transition which was previously investigated (2). The analysis of the (005) band showed that the (005) level is isolated, i.e., largely decoupled from the other vibrational states.

The HDO molecule is a nonsymmetric isotopomer of H₂O with a strongly different ratio between its harmonic frequencies as compared to the parent molecule. This results in a different resonance polyad scheme even for low-lying vibrational states. The large difference between the OD and OH stretching frequencies ($\omega_1 = 2823.9$ and $\omega_3 = 3893.40$ cm⁻¹, respectively)

prevents efficient Coriolis-type interaction in the HDO molecule and gives rise to a well-isolated sequence of the $(00V_3)$ vibrational states up to $V_3 = 5$. However, we have shown that the (004) state is slightly perturbed by a local resonance with the (052) highly excited bending state (1).

Little is known about the resonance interactions between the HDO rovibrational states. A Hamiltonian taking explicitly into account both Fermi and Coriolis interactions was set up for triatomic molecules of C_s symmetry and successfully applied to treat the resonance interactions between the (100) and (020) states (3) and between the (110) and (030) states (4) of HDO. The coupling scheme between the (101) and (021) states was investigated in Ref. (5), while the study of the [(210), (050), (130)] triad reveals an unusually strong high-order anharmonic resonance between the (210) state and the (050) bending state (6). All these polyads appear to be the consequence of the relation $\omega_1 \approx 2\omega_2$ ($2\omega_2 \approx 2887.44 \text{ cm}^{-1}$), which corresponds to a Fermi-resonance coupling. To our knowledge, no other treatment of the resonance coupling between higher vibrational states of HDO is available.

The (014) state under study has one additional bending quantum excited as compared to the (004) state previously analyzed (1), but this results in drastic changes in the resonance perturbations of the rotational sublevels: the forthcoming rotational analysis shows that all the energy levels with $K_a = 0,1$ are strongly perturbed. The perturbing partners of the (014) state will be assigned with the help of the recent high-accuracy *ab initio* calculations reported by Partridge and Schwenke (PS) (7).



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FIG. 1. Comparison of the overview of the stick spectrum of HDO (a) extracted from the ICLAS spectrum recorded with an equivalent path length of 12 km and a total vapor pressure of 13 Torr with the stick spectrum (b) calculated with the parameters of Tables 3, 5, and 8.

2. EXPERIMENT

The experimental apparatus for ICLAS has been previously described (8). The technical details and a very recent review of the results obtained by ICLAS in the field of overtone spectroscopy and optical diagnostics can be found in Ref. (9). 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. The intracavity sample cell was filled with a 1:1 mixture of H₂O and D₂O at a pressure of 13 Torr (94 hPa). This procedure is assumed to lead to a mixture of H₂O:HDO:D₂O in the proportion 1:2:1. The spectra were obtained with a generation time of 80 μ s corresponding to an equivalent absorption path length of 12 km. A Rhodamine 590 dye solution was used to record the spectrum between 14 980 and 17 100 cm⁻¹.

The spectral resolution of the high-resolution grating spectrograph dispersing the laser spectrum is about 0.03 cm⁻¹, close to the Doppler broadening (0.05-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 calibrated absolutely by the use of two reference lines. Lines due to H₂O (*10*) appearing superimposed on the HDO spectrum were used as references except in the region below 15100 cm⁻¹, where we used iodine absorption lines obtained by inserting an iodine cell on the laser beam outside the laser cavity. We estimate our wavenumber calibration to be accurate

to within 0.01 cm^{-1} , as will be confirmed by the ground state combination differences (GSCD) provided by the rotational analysis.

ICLAS is suitable for measuring accurate absorption intensity without any need of reference (see, e.g., Refs. (9, 11-13)). It requires, however, a careful study of the dependence of each absorption line intensity on the generation time (8). In the present study, we used a rough estimation of the line intensities provided by the peak depth of each line. This method leads to relatively strong deviations both for the stronger and the weaker lines which are systematically under- or overestimated, respectively. In particular, for the 10% weakest lines, the automatic procedure used for the determination of the absorption baseline might lead, in some cases, to a 100% overestimation of the peak depth. In spite of its limited accuracy, this information will, however, prove to be highly valuable for the spectral identification.

3. THEORETICAL TREATMENT OF THE SPECTRUM

A. The Spectrum Assignment

Overall, 742 absorption lines were measured in the 14 980–15 350 cm⁻¹ spectral region. Among them, 233 lines were attributed to H₂O (*10*). Figure 1 shows an overview of the stick spectrum limited to the HDO lines.

The first step of the assignment process consisted of predicting the $\nu_2 + 4\nu_3$ band transitions. The initial set of rotational and some quartic centrifugal distortion constants for the (014) state was estimated from PS's energy levels (7), while other high-order centrifugal distortion constants were constrained to the corresponding values of the (011) state (14). These parameters were then refined from the fitting to the experimental energy levels (see below) in parallel with the identification process. Estimations of the (014) state transition moment parameters were obtained as in Ref. (15) from the fitting to the experimental intensities of several tens of well-isolated absorption lines. The synthetic spectrum calculated with the above parameters was used in an adaptive program for automatic rovibrational spectra identification built on the basis of the pattern recognition theory (16). This program is a sort of expert system which searches for GSCD in the analyzed spectrum and chooses the best variant using several types of informative features as the number of lines reaching the upper level, the accuracy of the upper energy level determination, the proportionality of the observed and calculated intensities, as well as the differences between observed and calculated lines positions. The assignments of the lines as well as the experimental energy levels are stored into database which is renewed throughout the spectrum identification.

The final results of the assignment process detailed just below are the following: 313 of the measured absorption lines (hereafter the full number of assigned lines is given including a double weight for blended lines with double assignment) were attributed to transitions involving the (014) upper state. One hundred transitions related to the (142) and (0 12 0) highly excited upper states were found as a result of strong resonance interactions with the (014) state. Furthermore, eight transitions were assigned as resulting from accidental resonances between the (014) bright state and the (302), (411), and (062) states. Among about 130 weak absorption lines left to be assigned, 46 of them were finally attributed to the extremely weak $6\nu_1$ band, while 13 lines not included in the HITRAN database were identified as being due to H₂O. Finally, 72 (about 15%) weak lines remain unassigned.

To give some idea of the absolute experimental intensities of the assigned lines, our experimental and calculated relative intensities were normalized to the total HDO absorption intensity given by Partridge and Schwenke (7) for pure HDO at 296 K for the same spectral region. (Note that only lines reaching rovibrational levels with an energy lower than 15 730 cm⁻¹ were considered, as this energy is the upper limit of PS's line list available to us.)

The frequencies of the HDO absorption lines are presented in Table 1 along with their experimental and calculated intensities, those provided in Ref. (7) when available, and their rovibrational assignments. In a few cases, the assignment is only tentative and the corresponding line is preceded by T.

B. Energy Level Fitting

The upper state energy levels were obtained by adding the experimental rotational energy levels of the ground state (17)

to the assigned transitions. They are presented in Table 2 together with the (obs. - calc.) deviations, the experimental uncertainties, and the number of lines used in the determination of the given energy level. The deviation from PS's predictions, given also in Table 2, are negative with a magnitude generally less than 1 cm⁻¹ and a maximum value of 3 cm⁻¹.

Our first attempts to fit the energy levels of the (014) state as those of an isolated state failed to show that this state is, in fact, strongly perturbed: all the energy levels with $K_a = 0.1$ starting with J = 0 greatly deviate (up to 1.5 cm⁻¹) from their unperturbed positions. Furthermore, almost for each line involving a rotational level with $K_a = 0$ or 1, two additional lines were observed in the spectrum. The upper energy levels of these extra lines were derived with certainty from GSCD of several lines. The assignment of the perturbers on the basis of PS's predictions was difficult since, in many cases, the same rovibrational assignment is attached to two or even three different energy levels. In the case of the (014) state, for instance, two energy levels were given for each of the following rotational states: [000], [101], [202], and [404], and three energy levels were assigned to the [303] state. According to PS (7), the (302), (411), (222), (142), (062), (072), and even the (0 12 0) vibrational states are possible perturbers. However, the local character of the perturbations indicates that the perturbers should be some highly excited bending states, since for such states, the energy of the rotational sublevels increases very rapidly with K_a , and a crossing with the (014) energy levels can take place only for certain K_a values. From these considerations, the first perturber was assigned rather easily to the (142) vibrational state at 15 171.20 $\rm cm^{-1}$ (our estimation from the parameters given in Ref. (2) was $15 \ 193 \ \text{cm}^{-1}$).

It was more difficult to fix the second resonance partner of the (014) state, since the assignment of the (062), $(1\ 10\ 0)$, (091), and (0 12 0) states were frequently interchanged in PS's predictions. A similar difficulty was found in the assignment process of the perturber of the (004) state. Our analysis (1)showed that the (004) state is slightly perturbed by the (052) state, while this perturber is assigned as $(0 \ 11 \ 0)$ in Ref. (7). The estimations of the A rotational constant and of the centrifugal distortion constants for such highly excited states are not accurate enough to check PS's assignments. We proceeded then, step by step, starting from $J = 0,1,2, K_a = 0,1$ energy levels. We adopted the PS's value given in Table 3 for the vibrational energy, varied only the A constant, and then checked that the next energy levels were correctly predicted with the new A value. This process led us to assign the second resonance partner of (014) to the (0 12 0) pure bending state. The occurrence of such high-order resonance interactions may appear surprising. It was, however, experimentally proved for H₂O and theoretically interpreted as resulting from a rapid increase in the resonance coupling with the bending excitation (18-20). For the H₂O species, this coupling was estimated to vary exponentially with the sum of the bending quantum numbers of the resonating states (18).

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TABLE 1Wavenumbers, Intensities, and Rotational Assignments of the HDO
Absorption Lines between 14 980 and 15 350 cm⁻¹

Observed	<u> </u>	Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber	01-	(cm ⁻² /atm) D-£(7)	$J K_a K_c$	J K _a K _c	State	Wavenumber	0.	(cm ⁻² /atm	1) 1 D - 6 (7)	$J K_a K_c$	J K _a K _c	State
14981 792	6.9E-7	J Caic.	[Rel.(7)			1	(cm) 15032 240	3 9F-6	4 2E-6	4 2E-6	63.4	735	0.14
14982.275	1.0E-6	9.7E-7		844	945	0 1 4	15033.365	6.9E-7	6.7E-7	2.2E-7	101	202	6 0 0
14982.866	8.4E-7	5.1E-7		10 0 10	11 1 11	142	15035.112	5.0E-7	5.1E-7	1.5E-7	111	212	600
14983.242	1.5E-6	9.3E-7		936	1037	0 1 4	15035.695	6.1E-7	3.3E-7		918	937	014
14986.675	6.1E-7	6.7E-7	2.3E-7	312	413	600	15036.229	9.4E-7	9.3E-7	8.0E-7	707	818	0 1 4
14986.829	4.3E-/	4.2E-7	1.5E-/	321	422	6 0 0	15036.922	6.1E-6	5.9E-6	5.8E-6	707	808	014
14990 068	1.0E-0	1.3E-0		92.8	102.8	0 1 4	15037.898	1.3E-6	1.2E-6	1.0C-0	717	80.8	014
14991.960	1.5E-6	1.8E-6		918	1019	0 1 4	15038.903	4.5E-7	1.6E-7		973	972	0 1 4
14993.256	1.6E-6	7.6E-7		652	753	014	15038.903	4.5E-7	1.6E-7		972	973	014
14993.256	1.6E-6	7.6E-7		651	752	014	15039.073	7.6E-7					
14995.843	6.5E-7						15039.855	7.7E-7	3.1E-7		872	871	0 1 4
14996.069	3.0E-7	4 2E-7		826	937	1 4 2	15039.855	7.7E-7	3.1E-7		8/1	8/2	014
14997.208	8.0E-7	8.0E-7	2.6E-7	303	404	6 0 0	15040.755	1.7E-6	5.9E-7		771	770	0 1 4
14997.864	1.3E-6	1.4E-6		836	937	014	15040.755	1.7E-6	5.9E-7		770	771	0 1 4
14998.288	1.3E-6	1.0E-6		909	10 1 10	0 1 4	15041.537	6.3E-7					
14998.482	3.0E-6	1.5E-6		744	84 5	014	15041.774	2.1E-6	1.9E-6	2.0E-6	707	808	142
14998.482	3.0E-6	2.0E-6		7/2	844	014	15042.096	6.8E-6	6.3E-6	6.5E-6	624	72.5	0 1 4
14998.599	2.0E-0	2.1E-6		919	10 1 10	014	15044.398	7.1E-7	6 7E-6	69E-6	625	726	0 1 4
14998.793	1.3E-6	1.2E-6		919	10 0 10	0 1 4	15045.061	6.7E-7	0.72 0	0.72.0	02 5	120	014
14999.278	1.6E-6	1.7E-6		835	936	014	15045.703	5.4E-7	4.6E-7		817	836	0 1 4
15000.301	8.5E-7	7.6E-7	2.2E-7	313	414	600	15046.059	3.9E-7					
15001.321	8.0E-7	1 45 7		0.0.1			15046.467	4.3E-7	4.0E-7	6.2E-7	615	726	1 4 2
15001.953	5.1E-/	1.4E-/		881	880	0 1 4	15048.065	7.2E-6	8.0E-6	8.5E-6	615	716	0 1 4
15001.955	5.1E-7 6.7E-7	1.4E-7 5.5E-7		909	10 1 10	1 4 2	15048.402	4.4E-0 4.4E-6	1.9E-0 1.9E-6	2.0E-6 2.0E-6	441	542	014
15003.802	5.3E-7	5.1E-7		909	10 0 10	1 4 2	15048.468	5.6E-6	5.5E-6	5.6E-6	532	633	014
15005.404	4.0E-7	4.0E-7		919	10 0 10	1 4 2	15048.810	3.6E-7	2.6E-7		422	423	6 0 0
15006.320	5.8E-7	2.1E-7		515	532	0 12 0	15048.933	5.3E-6	5.5E-6	5.7E-6	533	634	014
15006.397	5.0E-7						15050.204	4.6E-7	4.0E-7	1.3E-7	000	101	600
15006.484	5.3E-7	5.5E-7		202	313	600	15050.465	6.7E-7	4.6E-7	1.4E-7	322	321	600
15006.484	3.3E-7 2.7E-6	5.1E-7 2.4E-6		313	404 927	0 1 4	15051.347	4.5E-7	2./E-/	1.3E-/	413	432	014
15009.080	3.0E-6	3.1E-6		827	928	014	15051.646	4.6E-7					
15009.486	5.1E-7	3.3E-7	9.9E-8	220	321	6 0 0	15051.921	5.8E-7	5.9E-7	2.6E-7	716	735	0 1 4
15010.907	3.6E-7	3.4E-7	9.8E-8	221	322	6 0 0	15053.177	2.6E-6	4.0E-6	2.3E-6	606	707	142
15011.573	3.9E-6	3.2E-6		817	918	0 1 4	15053.282	5.5E-7	4.6E-7	1.5E-7	321	322	6 0 0
15012.608	7.7E-7	4.2E-7		312	321	6 0 0	15054.464	7.2E-7	5.5E-7	2.7E-7	615	634	014
15013.905	9.2E-7	0./E-8	4 1E-7	735	836	142	15055.219	4.5E-6	5.9E-/	3.5E~/	60.6	717	014
15014.704	1.1E-6		1.1L /	717	836	4 1 1	15056.506	6.3E-6	8.0E-6	9.9E-6	60.6	707	014
15015.223	4.7E-6	2.1E-6	2.1E-6	643	744	0 1 4	15056.746	3.3E-6	9.3E-7	1.9E-7	616	707	0 1 4
15015.223	4.7E-6	2.1E-6	2.1E-6	642	743	0 1 4	15056.987	4.8E-7	8.4E-7	2.3E-7	221	220	6 0 0
15015.494	3.7E-6	2.9E-6	2.8E-6	734	835	0 1 4	15057.171	4.2E-7					
15015.541	3.3E-6	2.9E-6	2.4E-6	735	836	0 1 4	15057.597	6.6E-7	8.4E-7	2.3E-7	220	221	600
15010.004	4.4E+/ 7.4E-7	5 5E-7		404	413	6.00	15057.734	4.0E-7					
15017.564	5.9E-7	0.001		101	415	000	15058.780	8.3E-6	8.8E-6	9.5E-6	523	624	0 1 4
15017.776	1.5E-6	1.0E-6	1.1E-6	808	919	0 1 4	15059.003	6.1E-7	5.5E-7	3.1E-7	707	726	0 1 4
15018.137	4.1E-6	3.8E-6	3.8E-6	808	909	0 1 4	15059.744	3.7E-7					
15018.279	4.8E-6	4.2E-6	4.1E-6	818	919	0 1 4	15060.746	4.5E-7	5.5E-7	1.7E-7	111	110	6 0 0
15018.646	1.8E-6	1.3E-6	1.2E-6	818	909	014	15061.294	4.8E-7	0.2E.4	1.05.5	52.4	(25	0.1.4
15021.012	9.0E-7	5 1E-7		101	212	6.0.0	15063 331	0.0E-0	9.3E-0	1.0E-3 9.5E-7	524	717	1 4 2
15022.129	4.8E-7	2.0E-7		1019	1038	0 1 4	15063.848	5.6E-7	1.3E-7	1.2E-7	707	726	142
15023.227	6.6E-7	5.9E-7	3.9E-7	808	919	1 4 2	15065.055	1.0E-5	1.1E-5	1.2E-5	514	615	0 1 4
15023.574	1.3E-6	9.7E-7	6.5E-7	808	909	142	15065.194	6.4E-6	5.9E-6	6.2E-6	431	532	0 1 4
15025.156	4.3E-6	4.0E-6	4.0E-6	725	826	0 1 4	15065.496	6.2E-6	5.9E-6	6.3E-6	432	533	0 1 4
15025.590	6.2E-7	5.1E-7	3.4E-7	8 I 8 9 1 9	919	142	15065.644	8.8E-7	5.5E-7	1.6E - 7	110	111	600
15025.958	4.0E-/ 71E-7	J./E-/	1.96-/	0 I ð	909	142	15067.023	5.8E-7 6.7E-7					
15027.297	6.1E-6	4.6E-6	5.0E-6	726	827	0 1 4	15069.422	7.0E-7	1.6E-7	1.1E-7	505	61.6	0 1 4
15029.284	4.5E-7	4.6E-7	1.5E-7	110	211	6 0 0	15069.422	7.0E-7	2.6E-7	1.1E-7	616	707	0 12 0
15030.288	4.8E-6	5.1E-6	5.4E-6	716	817	014	15070.441	5.5E-7					
15030.867	3.9E-7	1.0E-7	A 15 1	414	431	1 4 2	15070.963	5.5E-7					
15031.862	7.2E-6	2.3E-6	2.4E-6	542	643	0 1 4	15071.500	7.6E-7	2.9E-7		964	963	014
15031.862	7.2E-0	2.4E-0 4 2F-6	2.4E-0 4 2E-6	541	734	0 1 4	15071.500	7.0E-7 6.7E-6	2.9E-7 63E-6	2 9F-6	903 505	904 606	014
15051.002	1.44-0	1,22-0	1.20-0	0,0,0		U 1 T	150/1./50	J. / L-0	0.50-0	2.70-0		000	

TABLE 1—Continued

Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber		(cm ⁻² /atm)	$J K_a K_c$	$J K_{a} K_{c}$	State	Wavenumber		(cm ⁻² /atm	l)	$J K_a K_c$	$J K_a K_c$	State
(cm ⁻¹)	Obs.	Calc.	Ref.(7)	L			(cm ⁻¹)	Obs.	Calc.	Ref.(7)	I		
15072.114	3.9E-6	4.6E-6	2.7E-6	515	616	0 12 0	15103.702	6.2E-7	2.4E-7	1 25 6	431	330	6 0 0
15072.524	1.2E-0 1.2E-6	5.9E-7		867	863	014	15105.878	2.0E+0	9.3E-6	0.8E-6	303	414	142
15072.524	1.2E-0	9.7E-6	1 3E-5	515	61.6	014	15104.032	1.4E-6	3.2E-0	7.8E-7	312	404	0120
15072.862	1.2E-5	<i></i> 0	4.4E-6	523	60.6	3 0 2	15105.820	1.4E-5	1.7E-5	2.0E-5	313	414	0 1 4
15073.525	2.4E-6	1.1E-6		762	761	0 1 4	15106.737	8.0E-6	7.6E-6	9.2E-6	313	404	0 12 0
15073.525	2.4E-6	1.1E-6		761	762	014	15107.055	6.1E-7	6.3E-7	1.7E-7	423	322	600
15074.434	5.8E-6	2.0E-6		661	660	014	15107.877	2.6E-7	8.0E-8		1148	1147	0 1 4
15074.434	5.8E-6	2.0E-6		660	661	014	15108.671	6.0E-7	6.7E-7		505	414	600
15074.434	5.8E-6	5.1E-6	6.8E-6	515	606	0 12 0	15108.782	5.4E-7	5.9E-7	1.6E-7	422	321	600
15074.774	4.5E-7	7.2E-7	3.4E-7	606	625	0 1 4	15108.913	5.4E-7	1.1E-6	3.0E-7	404	303	600
15075 144	4.9E-/	3.9E-/	1.3E-/	515	625	014	15109.547	8./E-6	8.4E-6	9.4E-6	220	321	0 1 4
15075.100	2.0E-0	4.2E-0	2.4E-0	422	523	014	15110.095	4.4C-0 83E7	4.02-0	4.9E-0	212	202	142
15076 469	5 8E-7	6 3E-7	4 2E-7	717	716	014	15110.474	8.5L-7	8.4E-6	94E-6	221	322	0 1 4
15077.857	7.1E-7	7.6E-7	3.6E-7	514	615	142	15112.118	6.5E-7	0.12.0	7.4L 0	221	522	014
15077.939	1.5E-6	1.4E-6	1.2E-6	505	616	142	15113.191	8.3E-7	9.7E-7	2.6E-7	515	414	6 0 0
15078.397	1.1E-5	1.1E-5	1.2E-5	423	524	0 1 4	15113.663	4.0E-7	6.3E-7	1.6E-7	524	423	600
15079.522	4.9E-7	4.2E-7	1.3E-7	101	000	600	15114:146	1.1E-5	1.2E-5	1.1E-5	211	312	014
15079.692	4.6E-7						15114.800	8.3E-7	1.8E-7		1047	1046	0 1 4
15080.258	1.1E-6	5.9E-7	8.7E-7	505	606	1 4 2	15114.800	8.3E-7	2.1E-7	1.7E-7	202	313	142
15080.473	4.6E-7						15114.902	8.5E-7	2.6E-7		431	422	600
15081.594	1.2E-5	1.4E-5	1.6E-5	413	514	0 1 4	15114.902	8.5E-7	1.0E-6	2.7E-7	505	404	600
15081.788	5.9E-6	4.6E-6	4.9E-6	330	431	0 1 4	15115.498	1.4E-6	1.4E-6	(05 (515	514	0 12 0
15081.918	5.4E-0	4.0E-0	4.9E-0	122	432	6 0 0	15115.879	3.0E-0	3.3E-0	0.8E-0	211	312	0120
15082.675	5.5E-7	5.1E-7	5.0E-7	515	616	1 4 2	15117.018	1.5E-0 8.6E-7	0.3E+7 4.2E-7	1.2E-0	212	212	0120
15084 445	4 5E-7	5.1E=7	1.5E-7	505	52.4	0 1 4	15117.018	1 3E-6	4.2E-7	8.2E-7	726	725	0120
15084.747	3.9E-7	0.027	1.021	000		Ů.	15117.400	1.2E-6	8.0E-7	6.4E-7	313	414	1 4 2
15084.991	2.8E-7	2.2E-7	1.4E-7	111	220	0 1 4	15119.677	1.1E-5	1.2E-5	1.3E-5	202	303	014
15086.354	6.4E-7	1.2E-6	7.8E-7	404	515	0 1 4	15121.153	1.3E-5	1.6E-5	1.9E-5	212	313	0 1 4
15087.853	5.5E-6	1.1E-6		515	524	0 1 4	15121.809	1.3E-6	1.1E-6		845	844	0 1 4
15087.853	5.5E-6	5.1E-6	4.7E-6	414	505	0 12 0	15122.333	4.6E-7					
15088.825	3.5E-7	5.6E-7	1.6E-7	212	111	6 0 0	15122.637	5.7E-7	6.7E-7	1.6E-7	707	606	600
15089.281	1.0E-5	1.4E-5	1.5E-5	414	515	0 1 4	15123.103	6.3E-7	9.3E-8		211	222	0 12 0
15090.266	8.4E-6	1.1E-5	1.3E-5	404	505	0 1 4	15123.416	2.0E-6	2.1E-6	0.05 (744	743	0 1 4
15091.378	9.3E-/	8.0E-/	2.3E-1 4.1E-6	202	101	0 0 0	15123.842	7.4E+6	7.2E-6	8.0E-6	202	303	142
15091.550	2.9E-0	5.0E-0	4.1E-0 5.6E-7	404	513	1 4 2	15124.011	4.0E-0 2.7E 6	3.9E-0	3.4E-0	643	642	0 1 4
15092.200	5.8E-7	5.9E-7	5.06-7	321	312	6 0 0	15124.934	3.7E-0	3.9E-0	3.4E-0	844	845	014
15092.586	8.7E-6	1.1E-5	1.3E-5	321	422	0 1 4	15125.550	8 1E-6	6.7E-6	6 3E-6	54 2	541	014
15092.762	5.2E-7	3.6E-7	1.7E-7	414	423	0 12 0	15125.571	7.8E-6	6.7E-6	6.3E-6	541	542	014
15092.998	5.8E-7						15125.781	1.1E-6	1.2E-7		826	743	014
15093.218	1.6E-6	2.7E-6	2.2E-6	414	505	0 1 4	15126.090	2.2E-6	1.6E-6	1.9E-6	212	303	0 12 0
15093.363	5.8E-7						15126.315	1.5E-5	1.2E-5	1.1E-5	44 I	440	0 1 4
15094.637	8.6E-6	1.1E-5	1.3E-5	322	423	0 1 4	15126.315	1.5E-5	1.2E-5	1.1E-5	440	441	0 1 4
15095.468	1.8E-6	1.5E-6	1.7E-6	404	505	142	15126.673	7.6E-7	1.4E-7		826	835	1 4 2
15096.583	4.6E-7						15126.845	5.8E-7					
15097.724	4.1E-/	1455	1.05.5	21.2	41.2	014	15127.280	7.8E-7	5.1E-7		945	946	0 1 4
15097.978	1.1E-3 3.6E-7	1.0E-J 3.7E-7	1.6E-3 2.4E-7	303	413	014	15127.412	9.3E-/	8.0E~/ 9.4E 7	2 OF 7	830	835	0 1 4
15099.070	6.0E-7	5.9E-7	2.46-7	827	826	014	15128.410	1.1E-0 1.2E-6	0.4C-7	3.9E-7	211	211	0120
15099.162	6.5E-7	4.6E-7		955	954	0 1 4	15120.004	4 3E-7	2.0E-7	8.6E-8	212	303	0 1 4
15099.692	4.8E-7	4.6E-7		954	955	0 1 4	15130.964	3.9E-7	B .0 E ,	0.02 0	212	505	014
15099.856	5.4E-7	5.9E-7		404	313	6 0 0	15131.382	9.9E-6	9.7E-6	1.2E-5	110	211	0 1 4
15100.185	9.9E-7	9.3E-7		854	853	0 1 4	15131.667	2.5E-6	1.9E-6	1.7E-6	625	624	0 1 4
15100.349	1.0E-6	9.3E-7		853	854	0 1 4	15131.873	3.2E-7	1.9E-7	1.1E-7	514	431	0 1 4
15100.494	5.4E-7	6.3E-7	4.2E-7	313	414	0 12 0	15132.168	2.1E-6	1.7E-6	2.0E-6	414	413	014
15100.688	7.7E-7	7.6E-7	6.4E-7	414	515	142	15132.439	3.4E-7	1.5E-7	. . –	808	725	0 1 4
15100.961	1.9E-7	1 95 4					15133.550	9.3E-7	6.7E-7	5.4E-7	212	313	1 4 2
15101.167	2.9E-6	1.7E-6		753	752	0 1 4	15133.761	5.2E-7		2.4E-7	735	734	062
15101.167	2.9E+0 4 1E 7	1./E-0 2.2E 7	25E7	152	133	014	15134.371	5.7E-7	110.4	1 25 5	717	134	4 1 1
15101.492	4.1C-/	2.2C-/	2.5E-7	513	322	0120	15135.093	1.1E-3 1.3E-6	1.1E-3 1.0E-4	1.2E-3	101	202	014
15102 102	5.8E-6	3 2F-6		652	651	014	15136.175	1.5E-0	1.96-0	1.2E-0	133	212	014
15102.102	5.8E-6	3.2E-6		651	652	0 1 4	15136 722	6.8E-7	5.1E-5	1.50-5	22.0	111	6.0.0
15102.994	9.3E-6	5.5E-6	4.9E-6	551	550	0 1 4	15139.461	3.5E-6	3.6E-6	3.0E-6	634	633	0 1 4
15102.994	9.3E-6	5.5E-6	4.9E-6	550	551	0 1 4	15139.822	7.1E-6	6.3E-6	7.2E-6	101	202	142
15103.461	5.9E-7	8.4E-7	2.3E-7	312	211	600	15141.358	5.8E-7	5.1E-7		322	211	600
15103.589	5.3E-7	2.4E-7		432	331	600	15142.037	6.1E-6	6.3E-6	5.9E-6	533	532	0 1 4

NAUMENKO AND CAMPARGUE

TABLE 1—Continu	ed
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Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber	Obe	(cm ⁻² /atm) D=f(7)	$J K_a K_c$	$J K_a K_c$	State	Wavenumber	Oha	(cm ⁻² /atm	$\Big $ Bof (7)	$J K_a K_c$	$J K_a K_c$	State
(cm ⁻)	4 6E-6	<u>3 8E-6</u>	3 5E-6	524	523	0.14	15202 129	2.9E-6	1 7E-6	2 3E-6	303	212	1 4 2
15143.495	9.9E-6	1.1E-5	1.1E-5	432	431	0 1 4	15202.751	1.0E-5	1.1E-5	1.1E-5	322	221	0 1 4
15143.814	7.5E-7	2.6E-7	5.9E-7	303	312	142	15203.454	4.5E-6	2.8E-6	2.7E-6	542	441	0 1 4
15144.123	1.0E-5	1.1E-5	1.1E-5	431	432	014	15203.454	4.5E-6	2.8E-6	2.7E-6	541	440	014
15144.363	1.6E-5	1.9E-5	1.9E-5	331	330	0 1 4	15204.082	1.4E-5	1.8E-5	2.0E-5	313	212	0 1 4
15144.461	1.8E-5	1.9E-5	1.9E-5	330	331	0 1 4	15205.157	1.9E-5	1.0E-5	1.1E-5	321	220	0 1 4
15144.461	1.8E-5	6.3E-6	5.9E-6	532	533	0 1 4	15206.132	6.1E-6	5.9E-6	6.1E-6	432	331	0 1 4
15144.692	5.8E-/	3.1E-/ 3.2E-6	3.0E-/ 3.3E-6	313	211	142	15206.549	0.3E-0 4.6E-7	3.9E-0	0.12-0	431	330	014
15146.004	4.1E-0	4.6E-7	J.JL-0	423	312	6 0 0	15208.039	1 1E-5	11E-5	1 1E-5	303	202	0 1 4
15146.298	3.5E-6	3.5E-6	3.0E-6	633	634	0 1 4	15210.035	2.3E-6	1.3E-6	1.12.5	753	652	0 1 4
15146.972	3.9E-7						15210.035	2.3E-6	1.3E-6		752	651	0 1 4
15149.104	9.0E-7	4.6E-7	3.4E-7	111	212	1 4 2	15210.720	9.1E-6	9.3E-6	1.1E-5	313	202	0 12 0
15150.207	6.8E-6	6.7E-6	6.7E-6	423	422	014	15210.940	5.1E-7	2.8E-7		964	863	0 1 4
15150.389	1.8E-6	1.7E-6	1.4E-6	734	735	0 1 4	15210.940	5.1E-7	2.8E-7		963	862	0 1 4
15150.596	8.0E-6	6.3E-6	7.1E-6	000	101	014	15212.370	5.4E-7	5.1E-7	3.2E-7	211	110	142
15151.228	7.3E-7	2.8E-7	2.5E-7	212	211	0120	15213.369	1.1E-6	1.4E-6	1.0E-6	615	616	0 1 4
15151.459	5.5E-/						15214.095	4.0E-0	J.1E-0	4.3E-0 2.1E-5	303	202	0142
15154 620	1 1E-5	1 2E-5	1 2E-5	322	321	0 1 4	15214 778	1.9E-5	2.0E-5	2.1E-5	414	313	0 1 4
15155.373	7.1E-6	5.9E-6	6.7E-6	212	211	0 1 4	15215.658	9.5E-7	5.1E-7	2.100	615	60.6	014
15155,434	5.1E-6	3.4E-6	3.9E-6	000	101	142	15215.658	9.5E-7	1.1E-6	7.2E-7	313	212	142
15156.785	1.6E-5	2.1E-5	2.3E-5	221	220	014	15216.037	4.9E-7	3.9E-8	6.5E-7	313	202	0 1 4
15157.032	6.9E-7	8.4E-7		835	836	014	15216.646	1.1E-5	1.5E-5	1.6E-5	423	322	0 1 4
15157.254	2.8E-7	7.2E-7	2.3E-7	111	110	0 12 0	15217.029	3.6E-6	3.0E-6	3.7E-6	404	313	1 4 2
15157.699	1.6E-5	2.1E-5	2.3E-5	220	221	0 1 4	15217.300	2.2E-7					
15159.033	1.1E-5	1.2E-5	1.2E-5	321	322	0 1 4	15218.312	3.7E-6	3.6E-6	3.3E-6	643	542	0 1 4
15161.803	1.3E-5	1.2E-3	1.4E-5	111	110	0 1 4	15218.483	7.9E-0	7.2E-0	0.2E-0	414	503	0120
15162.558	7.4E-0 1.1E-6	0.3E-0 1.2E-6	0.0E-0 5.5E-7	422	423	0120	15210.345	4.9E-0	5.0E-0 6.3E-7	3.3E-0 4.8E-7	322	303	014
15165 330	5.2E-7	4.2E-0	5.56-7	817	734	0120	15220.339	1.4E-5	1.5E-5	1.8E-5	404	303	014
15167.770	1.2E-5	1.2E-5	1.4E-5	110	111	0 1 4	15220.931	1.1E-5	8.4E-6	8.2E-6	533	432	0 1 4
15168.696	3.8E-6	3.6E-6	3.4E-6	523	524	014	15221.877	9.7E-7	1.0E-6	7.4E-7	423	404	0 1 4
15172.287	3.5E-7	6.3E-7		330	221	600	15222.455	1.0E-5	8.4E-6	8.1E-6	532	431	014
15172.486	5.6E - 6	4.6E-6	4.5E-6	211	212	014	15222.505	1.4E-5	1.5E-5	1.5E-5	422	321	014
15174.218	2.5E-6	2.0E-6	2.8E-6	211	212	0 12 0	15223.657	7.1E-7					
15174.756	6.4E-7	5.9E-7	3.8E-7	111	110	142	15223.815	1.4E-6	2.4E-6	7.5E-7	414	303	0 1 4
15175.554	3.9E-7	2.05.6	1.05 ((2)	(25	0.1.4	15224.033	3.5E-7	0.25 (105 (<i></i>		0.12.0
15177.342	2.5E-0	2.0E-0	1.8E-0	073	023 971	014	15224.343	3.7E-0	9.3E-0	1.9E-0	515	414	0120
15177.633	5.0E-7	8.0E-8		973	871	014	15224.760	2.1E-0	1.5E-0	0.21-7	854	753	014
15179 395	4.6E-7	0.0L-0		112	0 / 1	V 1 1	15224.882	L8E-6	1.1E-6		853	752	014
15179.577	6.0E-7	5.1E-7		432	321	.600	15225.108	1.5E-5	1.5E-5	2.1E-5	515	414	0 1 4
15180.578	4.7E-6	3.9E-6	4.1E-6	312	313	014	15226.086	3.3E-6	2.6E-6	3.5E-6	404	303	142
15181.276	8.3E-6	6.7E-6	7.3E-6	101	000	014	15226.162	1.5E-6	1.4E-6	9.1E-7	414	313	142
15181.884	9.9E-7	3.0E-7		762	661	014	15227.906	8.2E-6	1.1E-5	4.4E-6	505	404	014
15181.884	9.9E-7	3.0E-7		761	660	0 1 4	15228.060	6.3E-7		< 15 F			
15184.159	6.1E-7	3.7E-7		533	422	600	15228.898	1.1E+6	1.1E-6	6.4E-7	625	606	0 1 4
15184.054	0.3E-/	3 8E-6	446-6	101	0.0.0	1 4 2	15229.004	5.4E-0	1 4E 5	0.3E-0	523	404	3 0 2
15186 757	4 4F-7	2 1 F-7	4.4L-0	211	212	1 4 2	15229.090	2.4E-5	1.0E-5	1.0E-5	505	423	1 4 2
15187 608	7.2E-7	5.1E-7	3.5E-7	212	111	0 12 0	15230.180	2.7E-6	6 7E-7	3.2E-7	312	211	142
15187.846	1.9E-6	1.2E-6	9.0E-7	725	726	014	15230.352	1.8E-5	2.2E-5	2.3E-5	413	312	0 1 4
15189.391	5.3E-7	3.7E-7		532	423	600	15230.564	8.6E-6	8.8E-6	1.2E-5	515	404	0 12 0
15189.521	4.8E-7	8.4E-8		1138	1139	014	15231.025	2.5E-7	1.5E-7		1129	11 2 10	0 1 4
15190.450	2.8E-6	2.7E-6	2.6E-6	413	414	014	15231.324	3.5E-6	5.5E-6	1.2E-6	515	404	014
15191.739	1.3E-5	1.3E-5	1.4E-5	212	111	014	15232.750	4.6E-7					
15193.541	5.8E-7	1 05 ((= 2		0.1.4	15232.928	4.6E-7	2.45.7			(1 3	
15195.304	4.4E-0	1.0E-6		652	550	014	15233.110	3.3E-0	3.4E-6		/4 4	643	014
15195.504		1.0E-0	12E-5	2021	101	014	15233.393	9.0E-/	7 28-7	23E-6	60.6	515	0.14
15196 398	9.1E-7	3.5E-7	1.212	863	762	014	15234 011	1.4E-5	2.1F-5	1.7E-5	616	515	014
15196.398	9.1E-7	3.5E-7		862	761	014	15234.011	1.4E-5	3.4E-6	1.7L J	74.3	64 2	0 14
15196.870	4.8E-7	2.5E-7		633	524	6 0 0	15234.384	4.8E-6	7.6E-6	4.2E-6	606	505	142
15198.114	1.0E-5	9.7E-6	9.0E-6	211	110	014	15235.450	8.3E-6	8.4E-6	7.7E-6	634	533	0 1 4
15199.446	6.4E-7	6.7E-7		826	827	014	15235.810	1.3E-6	1.4E-6	8.9E-7	515	414	142
15199.653	7.3E-6	6.7E-6	7.4E-6	202	101	1 4 2	15236.408	1.8E-6	1.2E-6	1.9E-6	505	404	142
15199.851	4.5E-6	3.4E-6	3.3E-6	211	110	0120	15237.724	1.0E-5	1.5E-5	1.5E-5	606	505	014
15201.704	2.8E-0 1.0E 4	1.95-0	1.0E-0	514 515	515	0120	15237.939	1.2E-0 23E 7	1.2E-0	1.0E-0	010	505	014
15201.712	1.70-0	1.56-0	1.50-0	L	101	V 14 U	10200.902	4.JL-/					

TABLE 1—Continued

Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber		(cm ⁻² /atm)	$J K_a K_c$	J Ka Kc	State	Wavenumber		(cm ⁻² /atm)	J Ka Kc	J Ka Kc	State
(cm ⁻¹)	Obs.	Calc.	Ref.(7)				(cm ⁻¹)	Obs.	Calc.	Ref.(7)			
15239.408	8.2E-6	8.0E-6	7.6E-6	633	532	0 1 4	15265.710	7.4E-7	8.0E-7		10 1 10	909	1 4 2
15239.531	1.3E-6	8.0E-7		955	854	014	T 15265.947	1.9E-6	1.8E-6		12 1 12	11 0 11	014
15239.651	6.6E-7	8.0E-7		827	808	0 1 4	15266.347	1.3E-5	1.3E-5	1.2E-5	716	615	014
15239 848	3 9E-7	3.5E-7		937	918	0 1 4	T 15266.501	1.9E-6	1.6E-6		12 0 12	11111	014
15239 954	9 1E-7	8 0E-7		954	853	0 1 4	15267.446	2.0E-6	1.7E-6		945	844	0 1 4
15240 507	1.3E-5	1.6E-5	1.6E-5	523	422	0 1 4	T 15267 626	14E-6	1 1E-6		11.0.11	10 1 10	142
15240.837	1.3E-6	1.6E-6	3 9E-7	707	616	014	15268 535	1 1E-6	1.2E-6	1.0E-7	330	221	0 1 4
15240.074	1.3E-6	1.0E 0	8 2E-7	413	312	142	T 15269 420	92F-7	93E-7		13 0 13	12112	0 1 4
15240.574	1.2E-5	135-5	1 3E-5	62.5	524	014	15269 723	5 3E-6	5.5E-6		92.8	827	014
15241.807	1.2E-5	1.50-5	1.5E-5	717	61.6	014	15270 181	14F-6	0.000		, 20	02 /	• • •
15241.007	2 1E 6	1.50.5	1.5L-5 1.4E-6	61.6	515	1 1 2	15270.732	7 1E-7					
15241.924	2.1E+0	5.05 7	1.40-0	010	010	014	15270.752	8257	0 35 7	3 OF.7	615	514	1 4 2
15242.208	J.0E-/	1.95-7	1.00.5	707	717	014	15271.005	6.5E-7	2.3L-7	5.71-7	1156	1055	014
15243.134	1.1E-5	1.38-3	1.2E-3	707	716	014	15271.905	0.0E-7	2.0E-/		1150	1055	014
15243.200	1.3E-0	4.0E-/	1.0E-7	155	/ I U	1 4 2	15272.306	0.4E-7					
15243.266	1.3E-0	1.0E-0	9.0E-7	615	524	142	15273.147	4.2E-7	0.05.4		017	71 (0.1.4
15244.585	1.6E-3	2.1E-5	2.1E-5	514	413	014	152/3.382	7.8E-0	8.8E-0		817	/10	014
15245.242	4.6E-7	5.9E-7		928	909	014	15273.956	3.2E-6	3.3E-6	0.05.6	937	836	014
15245.670	9.7E-7	1.3E-6	3.8E-7	707	616	1 4 2	15274.715	9.5E-6	1.1E-5	9.8E-6	72.5	624	014
15246.619	4.7E-7	4.2E-7	1.8E-7	634	615	0 1 4	15276.014	1.3E-6	8.4E-7		1047	946	0 1 4
15247.879	2.9E-6	2.6E-6		845	744	0 1 4	15276.320	3.1E-6	3.5E-6		1029	928	0 1 4
15247.958	4.2E-6	4.1E-6	4.3E-6	707	606	142	15276.690	4.6E-6	4.6E-6		835	734	0 1 4
15248.120	2.2E-6	2.3E-6	9.5E-7	808	717	014	15278.482	5.0E-6	5.5E-6		918	817	014
15248.192	1.6E-6		9.6E - 7	735	634	062	15278.748	3.9E-7					
15248.632	9.3E-6	1.1E-5	1.0E-5	818	717	014	15281.756	1.7E-6	2.0E-6		11210	1029	014
15248.800	1.9E-6	3.8E-7		1019	10110	014	15282.169	3.1E-6	3.5E-6		1019	918	014
15248.800	1.9E-6		1.3E-7	717	634	4 1 1	15284.234	2.0E-6	2.0E-6		1038	937	014
15249.404	9.1E-6	9.7E-6	9.4E-6	808	707	014	15285.520	1.8E-6	2.0E-6		11 1 10	1019	0 1 4
15249.670	5.6E-6	6.7E-6	5.2E-6	735	634	014	15286.066	1.1E-6	1.1E-6		12211	11 2 10	014
15249.828	8.9E-7	1.6E-6	1.4E-6	717	616	1 4 2	T 15286.190	1.0E-6	1.0E-6		1046	945	0 1 4
15249.916	2.3E-6	2.9E-6	1.2E-6	818	707	014	15288.276	1.9E-6	1.5E-6	1.2E-6	422	303	014
15250.268	2.3E-6	2.6E-6		844	743	014	T 15288.276	1.9E-6	1.1E-6		12 1 11	11 1 10	0 1 4
15252.374	1.1E-5	1.2E-5	1.1E-5	726	625	0 1 4	15288.864	6.9E-7	5.1E-7		1148	1047	0 1 4
15253.570	1.0E-6	1.2E-6	4.1E-7	808	717	142	15289.270	6.6E-6	7.2E-6		826	725	0 1 4
15254 499	5.5E-6	6 3E-6		919	818	0 1 4	15290.126	4.6E-7					
15254 857	67E-6	5.9E-6		909	80.8	0 1 4	T 15290 642	6 1E-7	5 5E-7		13 1 12	12 1 11	0 1 4
15254.857	6.7E-6	2.5E-6	1 7E-6	808	707	1 4 2	15291 970	5 0F-7	0.00				• • •
15255 189	3.5E-6	3.3E-6	1.72.0	919	80.8	014	15293.058	1 3E-6	1 1E-6		1139	1038	0 1 4
15255.551	5.8E-7	5.1E-7		1055	954	014	15295.030	3.0F-6	3.0E-6		036	835	014
15255.051	1.2E 6	135-6	01E-7	818	717	1 1 2	15299.041	2 0E-7	J.0L-0		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	055	014
15255.755	1.20-0	1.56-6	1.7E-5	615	514	014	15300 143	1.4E-6	5 5E-7		12310	113.0	0.14
15250.745	5 9E 7	5.55.7	1757	010	707	1 4 2	15201 282	1.4L-0 11E 6	1 DE 6		027	876	014
15257.224	J.0E-/	1.20-7	1.7E-7	514	107	1 4 2	15301.262	4.1E-0	4.2E-0		921	020	014
15257.557	1.1E-0	1.5E-0	0.0E-/	774	413	0 1 4	15303.243	0 412 7					
15257.019	0./E-0	0./E-0	0.06-0	() 4	633	014	15305./44	0.4E-7					
15258.213	1.6E-5	1.35-5	1.3E-3	024	323	014	15305.470	4.2E-7	A 70 7			10 2 10	0.1.4
15259.132	3.9E-6	2.8E-6		10 0 10	919	014	1 15305.777	6.1E-/	2./E-/		13311	12 3 10	0 1 4
15259.497	3.3E-6	2.6E-6		10 0 10	909	014	15306.120	6./E-/	A (E) (
15259.497	3.3E-6	2.9E-6		10110	919	014	15309.893	2.6E-6	2.4E-6		10.2.8	927	0 1 4
15259.856	3.8E-6	3.3E-6		10 1 10	909	0 1 4	15312.166	1.9E-6	1.6E-6	1.3E-6	523	404	0 1 4
15260.242	1.4E-6	1.5E-6		909	808	142	15313.902	2.0E-6	1.8E-6		1037	936	0 1 4
15261.091	8.5E-7	9.7E-7		919	818	142	15315.307	2.8E-6	1.2E-6		1129	1028	014
15261.544	1.8E-6	9.7E-7		826	735	142	15317.349	3.1E-7					
15261.714	8.2E-6	8.4E-6		827	726	014	15318.003	6.7E-7	5.9E-7		12 2 10	1129	014
15262.281	4.7E-6	4.1E-6		836	735	014	T 15318.961	5.7E-7	2.7E-7		13 2 11	12 2 10	014
15262.281	4.7E-6	1.8E-6		946	845	014	15323.803	8.0E-7					
15263.088	2.6E-6	2.3E-6		11 0 11	10110	014	15329.459	8.8E-7	9.3E-7		1138	1037	0 1 4
15263.274	3.6E-7	1.1E-6		11011	10 0 10	014	15336.656	5.8E-7					
15263.707	6.4E-7	1.2E-6		11 1 11	10110	014	15336.823	6.7E-7					
15263.899	2.8E-6	2.6E-6		11 1 11	10 0 10	014	15338.773	4.8E-7	3.7E-7	1.6E-7	432	313	014
15264.159	1.4E-6	1.4E-6		10 0 10	919	142	15340.260	1.4E-6	1.3E-6	8.5E-7	624	505	0 1 4
15264.510	7.4E-7	9.3E-7		10010	909	142	15344.089	5.0E-7					
15265.351	5.0E-7	5.9E-7		10 1 10	919	1 4 2	15348.544	1.2E-6	1.4E-6	8.4E-7	<u>633</u>	514	0 1 4

Note. The experimental, calculated, and predicted (7) intensities are given in cm⁻²/atm at 296 K and correspond to pure HDO. The total calculated and experimental intensities of the HDO absorption are normalized (see text) to the total HDO intensity predicted in Ref. (7). *T* denotes tentative assignment.

After the determination of the two main resonance partners of the (014) state, we fitted the energy levels of all three interacting states. The effective rotational Hamiltonian was taken as

$$H = \sum_{v,v'} |v\rangle H_{vv'} \langle v'|, \qquad [1]$$

where v and v' are the different vibrational states of the triad.

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TABLE 2 Rotational Energy Levels (cm⁻¹) of the [(014), (142), and (0 12 0)] Triad of HDO

		(014)						(014)			
JK_aK_c	Eobs	obscalc.	σ	Ν	Δ	JK_aK_c	Eobs	obscalc.	σ	Ν	Δ
000	15166.104	0.022		1	-0.43	753	15919.191	0.016	0.010	2	
101	15181.271	0.018	0.005	2	-0.41	752	15919.188	-0.019	0.014	2	
111	15194.301	-0.019	0.001	2	-0.51	762	16054.664	0.036	0.011	2	
110	15197.573	-0.045	0.006	2	-0.50	761	16054.664	0.035	0.011	2	
202	15211.005	-0.017	0.002	2	-0.43	771	16212.287	-0.017		1	
212	15221.550	-0.003	0.006	3	-0.51	770	16212.287	-0.017		1	
211	15230.610	0.059	0.002	3	-0.41	808	15652.565	-0.014	0.002	5	-2.07
221	15266.046	-0.020	0.008	2	-0.51	818	15653.075	-0.024	0.003	4	-2.04
220	15266.618	-0.019	0.007	2	-0.51	817	15747.310	0.054	0.010	3	
303	15254.209	-0.016	0.002	3	-0.39	827	15752.161	0.029	0.014	4	
313	15262.210	0.045	0.006	4	-0.51	826	15809.394	-0.036	0.001	3	
312	15280.964	0.017	0.003	3	-0.51	836	15839.208	-0.071	0.019	3	
322	15311.678	-0.015	0.005	4	-0.51	835	15858.658	-0.090	0.009	3	
321	15314.423	-0.004	0.002	3	-0.55	845	15931.203	-0.025	0.001	2	
331	15377.410	-0.006	0.004	2	-0.52	844	15933.896	0.087	0.013	3	
330	15377.471	-0.010	0.010	3	-0.49	854	16042.757	-0.001	0.010	2	
404	15312.215	-0.039	0.003	3	-0.50	853	16042.888	-0.009	0.007	2	
414	15315.152	-0.070	0.008	4	-0.67	863	16177.527	0.003	0.001	2	
413	15346.827	0.003	0.008	4	-0.55	862	16177.527	-0.000	0.001	2	
423	15372.036	-0.009	0.004	4	-0.55	872	16334.691	0.001		1	
422	15379.576	-0.022	0.004	3	-0.70	871	16334.691	0.001		1	
432	15439.163	0.005	0.006	4	-0.66	909	15767.397	0.005	0.017	3	
431	15439.605	0.002	0.004	3	-0.52	919	15767.713	-0.021	0.007	4	
441	15528.645	-0.003	0.001	2	-0.49	918	15877.055	0.079	0.008	3	
440	15528.653	-0.001	0.008	2	-0.63	928	15879.661	0.031	0.012	3	
505	15378.057	0.009	0.005	2	-0.45	927	15954.358	0.047	0.012	2	
515	15381.484	0.019	0.005	6	-0.89	937	15975.580	0.043	0.004	2	
514	15427.563	0.008	0.008	4	-0.69	936	16007.792	0.031	0.019	2	
524	15446.740	0.007	0.008	3	-0.67	946	16070.844	-0.040	0.000	1	
523	15462.332	-0.008	0.007	4	-1.04	945	16076.848	-0.109	0.009	2	
533	15516.438	0.014	0.014	3	-1.00	955	16182.056	-0.013	0.007	2	
532	15518.130	0.005	0.002	3	-0.67	954	16182.504	-0.027	0.012	2	
542	15605.709	0.001	0.012	2	-0.02	904	16315.942	-0.025	0.002	2	
541	15005.823	0.001	0.009	2	-0.94	903	16472 472	-0.044	0.004	2	
550	15718.903	0.009		1	-0.89	973	16472.472	0.003	0.005	2	
*606	15/18.905	0.000	0.010	5	1 1 8	10010	15803.024	0.021	0.012	2	
616	15450 893	0.002	0.015	5	-1.10	10110	15804 286	-0.031	0.001	2	
615	15521 983	0.015	0.013	5	-0.92	101.0	16017 914	-0.131	0.002	3	
625	15535 222	0.017	0.005	4	-0.89	10 2 9	16019 417	-0.191	0.000	1	
624	15562 213	0.020	0.016	4	-1.55	10.2.8	16111 537	-0.000		1	
634	15609 128	0.023	0.010	4	-1.48	10.3.8	16125 602	-0.028		1	
633	15613.818	0.033	0.005	3	-0.88	1037	16173.295	0.002		1	
643	15698.561	0.002	0.015	3	-0.94	1047	16225.591	-0.002		1	
642	15698.820	-0.001	0.013	3	-1.43	10 5 5	16338.438	0.035		1	
652	15811.269	0.004	0.004	3		*11011	16032.205		0.001	2	
651	15811.270	-0.000	0.002	3		11111	16032.826	0.070	0.002	2	
661	15947.225	-0.000		1		11 1 10	16170.585	-0.042		1	
660	15947.225	-0.000		1		11 2 10	16171.332	0.011		1	
707	15549.441	-0.081	0.008	5	-1.59	1129	16280.154	0.000	0.004	2	
717	15550.415	-0.016	0.006	3	-1.65	1139	16288.851	0.029		1	
716	15628.844	0.024	0.013	3	-1.06	1138	16354.028	-0.016		1	
726	15637.246	0.033	0.003	3	-1.04	1148	16395.122	0.011	0.006	2	
725	15678.261	-0.011	0.012	3	-1.97	1156	16510.994	0.046		1	
*735	15717.181		0.012	4	-1.67	12211	16335.191	-0.000		1	
734	15727.289	0.027	0.004	3	-1.05	12210	16459.687	0.035		1	
744	15807.026	-0.035	0.015	3		12 3 10	16464.653	-0.019		1	
743	15807.987	0.004	0.005	2		l					

 TABLE 2—Continued

		(142)					(0.12	2 0)		
JK _a K _c	Eobs	obscalc.	σ	N	Δ	Eobs	obscalc.	σ	N	Δ
000	15170.943	0.013		1	-0.26					
101	15185.996	0.004	0.001	2	-0.25					
111	15207.242	0.034	0.011	2	-0.10	15189.750	-0.009		1	-0.09
110	15210.876	0.029		1	-0.07	15194.679	0.012	0.009	2	-0.12
202	15215.167	-0.013	0.006	2	-0.26					
212	15233.941	0.007		1	-0.13	15217.416	0.009	0.004	5	-0.14
211	15244.876	-0.045	0.007	3	-0.05	15232.344	-0.027	0.003	3	-0.25
303	15260.258	-0.050	0.005	4	-0.30					
313	15273.784	-0.009	0.002	-2	-0.19	15256.885	-0.011	0.007	4	-0.31
312						15287.170	0.044		1	-0.17
404	15317.416	0.051	0.002	4	-0.42					
414	15326.555	-0.022	0.001	2	-0.34	15309.805	0.015	0.006	3	-0.41
413	15357.436	-0.063	0.000	2	-0.23					
505	15386.564	-0.008	0.006	4	-0.59					
515	15392.207	0.016	0.014	2	-0.50	15380.727	0.007	0.005	5	-0.67
514	15440.352	-0.004	0.012	2	-0.36					
*606	15456.334		0.004	2	-1.00					
616	15467.783	0.005	0.006	2	-0.91					
615	15536.899	0.040	0.003	3	-0.50					
*707	15554.281		0.007	4	-1.37					
717	15558.443	0.035		1	-1.03					
808	15658.014	-0.013	0.007	4	-2.36					
818	15660.388	-0.018	0.007	4	-2.31					
826	15838.467	0.009	0.015	3						
909	15772.755	-0.001	0.017	3						
919	15774.316	0.012	0.018	2						
$10\ 0\ 10$	15898.944	0.040	0.006	2						
10 1 10	15900.140	-0.072	0.002	2						
		(302)								
523	15379.167		0.008	2	-0.35					
		(411)								
717	15716.323		0.008	3	-2.97					
		(062)								
735	15715.725		0.010	3	-1.58					

Note. Asterisks denote the energy levels excluded from the fitting. σ denotes the experimental uncertainty of the energy levels given in cm⁻¹. *N* is the number of lines sharing the same upper level. Δ is the difference between the experimental energy levels and the predictions of Ref. (7) (in cm⁻¹).

We evaluated the diagonal H_{vv} operators in the form of Pade– Borel approximants (21, 22). This approach is suitable in our case as the interaction involves highly excited bending states with large centrifugal distortion effects. Off-diagonal H_{vv} operators include both Fermi- and Coriolis-type terms (3)

$$F_{vv'} = F_0^{vv'} + F_k^{vv'} J_z^2 + F_j^{vv'} J^2 + F_{xy}^{vv'} J_{xy}^2$$
[2]

$$C_{vv'} = C_{y}^{vv'} i J_{y} + C_{xz}^{vv'} \{J_{x}, J_{z}\}.$$
[3]

Finally, by using 29 varied parameters, 145 energy levels were fitted with an rms deviation of 0.038 cm^{-1} . This value should be compared to an average experimental uncertainty of 0.007

cm⁻¹ of the energy levels derived from the combination difference of two or more lines.

The set of spectroscopic parameters obtained from the fitting is presented in Table 3 together with 68% confidence intervals. The values of the nonvaried parameters of the (014) and (142) states were fixed to the corresponding values of the (011) and (040) states (14), respectively. The fixed values of the parameters of (0 12 0) state were derived from the fitting to the predicted energy levels (7) or extrapolated from the lower bending states (7). The high bending excitation of the (0 12 0) state as well as the absence of experimental energy levels for K_a larger than one prevents the satisfactory evaluation of its centrifugal distortion parameters. Strong resonance interac-

TABLE	3
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Spectroscopic Constants of the (014), (142), and (0 12 0) States of HDO (in cm⁻¹) (see text)

(0	0 1 4)	(1 4 2)	(0 12 0)	
$E_{\nu} = \frac{(0)}{15167.7615(1)}$ $A = 20.87041(360)$ $B = 9.216189(900)$ $C = 6.008411(800)$ $\Delta_k = 1.5474(210) \times \Delta_{ik}$ $\Delta_i = 4.4272(450) \times \Delta_i$ $\Delta_i = 4.4272(450) \times \Delta_i$ $A_i = 4.4272(450) \times \Delta_i$	80) $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$ $80)$	(1 4 2) 15169.2494(410) 30.8448(690) 9.30065(310) 5.83460(200) 2.9730(520) ×10 ⁻¹ 5.6×10 ⁻⁴ -4.617(190) ×10 ⁻³ 5.024(100) ×10 ⁻⁴ 5.1×10 ⁻³ -9.5×10 ⁻⁵ 7.0×10 ⁻⁵	$(0 \ 12 \ 0)$ 14565.47 664.5655(820) 11.4149(120) 4.52058(590) 64.0 -1.2×10 ⁻² -6.633(130) ×10 ⁻³ 4.0×10 ⁻¹ 9.0×10 ⁻⁴ 31.0	

Coupling constants									
	F _o	F _k	F_j	F _{XY}	$C_{\mathcal{Y}}$				
(1 4 2)-(0 1 4)	-2.3067(220)		1.835(460) ×10 ⁻³		8.459(640) ×10 ⁻²				
(0 12 0)-(0 1 4)					-2.861(740) ×10 ⁻²				
(0 12 0)-(1 4 2)		-4.431(120)	2.381(570) ×10 ⁻²	-3.589(560) ×10 ⁻²	7.7825(660) ×10 ⁻¹				

tions in the triad as well as the influence of other dark states not included in the fitting are also responsible for some distortions in the values and signs of the derived parameters of the (142) and (0 12 0) states. These parameters, especially those of the (0 12 0) state, should be considered as effective parameters allowing the satisfactory reproduction of the energy levels connected to the (014) state. In the next section, we will show that this set of parameters is, however, accurate enough to trace the intensity redistribution from the $\nu_2 + 4\nu_3$ band transitions to the resonance line partners of the $\nu_1 + 4\nu_2 + 2\nu_3$ and $12\nu_2$ bands.

The fitting process showed that the resonance interactions within the triad are very strong for the $K_a = 0.1$ energy levels with mixing coefficients up to 50%. In some cases, the mixing coefficients were nearly equal for all three states resulting in an ambiguous vibrational assignment. Some examples of strongly mixed rotational levels are given in Table 4. To show the importance of the Fermi and Coriolis interactions, both even and odd K_a contributions are given. The value of the F_0 vibrational parameter coupling the (014) and (142) states is such that it induces an important vibrational mixing of the wavefunctions of the [000] rotationless state and consequently, a strengthening of the $[101] \leftarrow [000]$ rotational transition of the $\nu_1 + 4\nu_2 + 2\nu_3$ band. This predicted transition was indeed found in the spectrum at 15 155.435 cm^{-1} with a reasonable agreement between calculated (3.4 \times 10⁻⁶ cm⁻²/atm) and observed (5.1 \times 10⁻⁶ cm⁻²/atm) intensities.

TABLE 4 Examples of the Resonance Mixing between the Rotational States of the [(014), (142), (0 12 0)] Triad of HDO

			Mixing coefficients in %						
$V_1V_2V_3$	$J K_a K_c$	E_{obs} (cm ⁻¹)	(014	4)	(142	2)	(0 12	0)	
			e	0	e	0	е	0	
0 1 4	000	15166.104	65.3	0.0	34.7	0.0	0.0	0.0	
1 4 2	000	15170.943	34.7	0.0	65.3	0.0	0.0	0.0	
0 1 4	101	15181.271	63.7	0.0	36.0	0.1	0.0	0.3	
1 4 2	101	15185.996	36.0	0.0	61.5	0.1	0.0	2.4	
0 12 0	111	15189.750	0.3	1.8	2.4	7.7	0.0	87.7	
0 12 0	1 1 0	15194.679	0.0	5.4	0.0	10.3	0.0	84.3	
0 1 4	202	15211.005	59.8	0.0	38.0	0.1	0.0	2.1	
0 1 4	2 1 1	15230.610	0.0	67.3	0.0	10.5	0.0	22.2	
1 4 2	202	15215.167	33.3	0.1	34.8	1.8	0.0	30.0	
0 12 0	2 1 2	15217.416	6.8	2.0	26.8	5.7	0.0	58.7	
0 12 0	2 1 1	15232.344	0.0	30.2	0.0	4.8	0.0	64.9	
0 1 4	303	15254.209	45.8	0.0	38.6	0.9	0.0	14.6	
1 4 2	303	15260.258	17.1	8.8	53.8	3.9	0.0	16.4	
0 12 0	313	15256.885	36.2	0.6	2.6	3.8	0.0	56.9	
0 12 0	312	15287.170	0.0	4.5	0.1	27.7	0.0	67.8	
0 1 4	404	15312.215	56.8	1.2	0.0	3.1	0.0	38.9	
1 4 2	404	15317.416	11.3	11.1	57.5	1.4	0.0	18.7	
0 12 0	4 1 4	15309.805	28.1	0.1	34.3	2.4	0.0	35.1	
0 1 4	505	15378.057	42.6	0.1	34.2	2.0	0.0	21.2	
0 1 4	515	15381.484	10.2	76.2	5.9	2.4	0.0	5.3	
1 4 2	505	15386.564	5.9	4.6	54.2	9.8	0.0	25.5	
0 12 0	515	15380.727	41.0	15.5	3.2	6.3	0.0	33.9	
0 1 4	606	15459.660	68.3	0.1	26.4	0.8	0.0	4.5	
1 4 2	606	15456.334	30.4	0.1	43.5	2.4	0.0	23.7	
1 4 2	616	15467.783	0.4	7.4	15.2	65.8	0.0	11.3	
0 1 4	707	15549.441	76.9	0.6	21.0	0.4	0.0	1.1	
1 4 2	707	15554.281	21.9	0.5	69.1	1.2	0.0	7.3	

			-,		
	(01	4)	(142	2)	(0 12 0)
N^{a}	A-type	B-type	A-type	<i>B</i> -type	A-type
1	$9.8113(980) \times 10^{-5}$				
2	$1.0978(950) \times 10^{-7}$		$-9.88(100) \times 10^{-8}$		
3					$4.308(470) \times 10^{-6}$
4		5.794(280) ×10 ⁻⁶			
5	$1.039(190) \times 10^{-7}$	2.5397(800) ×10 ⁻⁶		$-3.262(660) \times 10^{-7}$	
6					$2.137(380) \times 10^{-6}$
7	$-4.140(370) \times 10^{-7}$				
8			$-1.342(160) \times 10^{-7}$	$8.09(270) \times 10^{-8}$	
Number		5	5	2	10
of Lines	23	5		3	10
δ^{b}	13.7	7%	15.	15.6%	

TABLE 5 Examples of Intensity Redistribution between Transitions Involving the Interacting Energy Levels of the (014), (142), and (0 12 0) Vibrational States of HDO

^{*a*} Numbering of the parameters (from 1 to 8) as defined in Ref. (15). ^{*b*} $\delta = | \mathbf{I}_{obs} - \mathbf{I}_{calc} | / \mathbf{I}_{obs}$ in percent.

It is worth noting that the $(014)-(0\ 12\ 0)$ interaction is mostly indirect, i.e., mediated by the (142) state which is strongly coupled to the (014) state on one side and to the $(0\ 12\ 0)$ level on the other. Only one resonance parameter, C_y , was varied for the $(014)-(0\ 12\ 0)$ interaction, whereas the $(0\ 12\ 0)-(142)$ interaction involves both Fermi- and Coriolis-type couplings. Even if the Coriolis parameter C_y (014)–(0 12 0) is constrained to 0, the mixing coefficient between some rotational sublevels of these two vibrational states reaches 38%, indicating that the direct contribution to the coupling is weak.

A few energy levels of the (014) and (142) states, marked by * in Table 2, appeared to be perturbed by extra local interactions, and so were excluded from the above fitting procedure. In some cases, the interaction was strong enough to give rise to several extra lines. On the basis of PS's predictions, we were able to assign three perturbers to the rotational sublevels of the (302), (411), and (062) vibrational states (see Table 2).

C. Line Intensity Considerations

In spite of their limited accuracy, our experimental intensities will allow us to discuss quantitatively the line-intensity redistribution. It is interesting to note that all the transitions involving unperturbed energy levels of the (014) state with $K_a \ge 2$ are exclusively of A type. In the process of the spectrum assignment, it appeared that both A- and B-type transitions involving perturbed energy levels with $K_a = 0,1$ were found with significant intensity, well consistent with PS's predictions, not only when the upper state was the vibrational resonance partner but also for the (014) bright state itself. This interesting effect is due to the coexistence of Fermi- and Coriolis-type interactions between the vibrational states of C_s symmetry.

When the energy levels of all three vibrational states were

fitted together and the wavefunctions containing the different resonance contributions were obtained, the intensity calculations were performed using the dipole moment parameters of the (014) state obtained from the fitting of unperturbed A-type transition intensities only. Assuming zero dipole-moment parameters for the (142) and (0 12 0) dark states, a rather good agreement between the calculated and experimental intensities was achieved for the A-type transitions of the three states, confirming that the (142) and (0 12 0) transition intensities are borrowed from the $\nu_2 + 4\nu_3$ band. At this step, the calculations predict an intensity transfer toward some *B*-type transitions, but these transitions are calculated to be significantly weaker than observed. In the final step, some dipole moment parameters of the (142) and (0 12 0) states as well as two parameters of the (014) state responsible for *B*-type transitions were allowed to vary in order to achieve a better coincidence with the experimental values. The 12 transformed transition moment parameters obtained from the fitting to 306 experimental line intensities with a partition function equal to 144.1 at 296 K are listed in Table 5. The numbering of the parameters (from 1 to 8) is the same as defined in Ref. (15). The average deviation between the calculated and experimental intensities is 14.1%, which is satisfactory considering our experimental accuracy. Figure 1 (overview) and 2 (expanded region) show the excellent agreement between the simulated and experimental spectra (see also Table 1). However, some calculated B-type transitions involving perturbed energy levels are still weaker than for the experimental data (see Table 1). The good agreement achieved, on average, between the calculated and observed intensities supports the resonance interaction scheme deduced from the energy level analysis. An example of resonance intensity redistribution between transitions involving three interacting levels is provided in Table 6. For instance, the sum



FIG. 2. Comparison of (a) the ICLAS spectrum with (b) the stick spectrum calculated with the parameters of Tables 3, 5, and 8, and (c) with the predictions of Partridge and Schwenke (7). The crosses (+) mark the H₂O lines (*10*).

 $(4.85 \times 10^{-5} \text{ cm}^{-2}/\text{atm})$ of the experimental intensities of *A*and *B*-type transitions involving the [404] (014), [404] (142), and [414] (0 12 0) interacting states is very close to the sum $(4.5 \times 10^{-5} \text{ cm}^{-2}/\text{atm})$ of unperturbed *A*-type transitions involving the [404] (014) bright level.

D. The $6v_1$ Band

In the final stage, 46 unassigned lines were attributed to the $6\nu_1$ band transitions. These transitions are extremely weak, but the following arguments make this assignment the most reasonable. In accordance with the predictions of Ref. (7), the (600) vibrational state can be considered isolated for small *J*

numbers, excluding [221] and [220] rovibrational levels which seem to be perturbed by a resonance interaction with sublevels of the (062) vibrational state. As a result of the GSCD search, several experimental energy levels with low *J* numbers were found in the spectrum from two or three lines. These energy lines were then used to determine the band origin which was found to be 0.74 cm⁻¹ higher than PS's prediction. The comparison of the observed and calculated intensities of the transitions involved in GSCD allowed us to give a value of 2.0×10^{-5} D for the ⁶⁰⁰ μ_1 transition moment parameter both for *A*and for *B*-type transitions, providing thus, line intensity predictions. In this way, we could finally determine 27 experi-

 TABLE 6

 Transition Moment Parameters (in D) for the (014), (142), and (0 12 0) Vibrational States of HDO

	Upper level [404] (014) 15312.215 cm ⁻¹				Upper level [404] (142) 15317.416 cm ⁻¹				Upper level [414] (0 12 0) 15309.805 cm ⁻¹				
Lower level	Obs. Wavenumber	Intensity (10 ⁻⁵ cm ⁻² /atm)			Obs. Wavenumber	Intensity (10 ⁻⁵ cm ⁻² /atm)		Obs. Wavenumber	Intensity (10 ⁻⁵ cm ⁻² /atm)				
J K _a K _c	(cm ⁻¹)	Unp.	Obs.	Calc.	Ref.(6)	(cm ⁻¹)	Obs.	Calc.	Ref.(6)	(cm ⁻¹)	Obs.	Calc.	Ref.(6)
303	15220.885	2.7	1.4	1.5	1.8	15226.085	0.33	0.26	0.35	15218.483	0.79	0.72	0.62
505	15090.266	1.8	0.84	1.1	1.3	15095.468	0.18	0.15	0.17	15087.853	0.55	0.51	0.47
515	15086.354	-	0.06	0.12	0.08	15091.550	0.29	0.30	0.41				
313						15217.029	0.36	0.30	0.37				
423										15092.762	0.05	0.04	0.02
Total		4.5	2.30	2.72	3.18		1.16	1.01	1.30		1.39	1.27	1.11

TABLE 7								
Rotational Energy Levels (cm ⁻¹) of the (600)	Vibrational	State of HDO					

J Ka Kc	E_{obs}	obscalc.	σ	N	Δ	$J K_a K_c$	Eobs	obscalc.	σ	N	Δ
000	15065.712	-0.024		1	0.74	404	15200.247	-0.011	0.004	3	0.74
101	15079.535	-0.006	0.008	4	0.76	413	15228.579	0.003		1	0.74
111	15093.241	0.002	0.002	2	0.72	423	15262.455	0.014	0.011	2	0.72
110	15095.460	0.041	0.008	2	0.75	422	15265.853	0.030	0.007	3	0.72
202	15106.881	-0.023	0.006	2	0.75	432	15336.627	-0.006	0.014	2	0.65
2 1 2	15118.634	-0.025		1	0.69	431	15336.746	0.000	0.008	2	0.66
*2 2 1	15166.276		0.020	2	0.66	505	15265.056	0.006	0.003	2	0.73
*2 2 0	15166.535		0.012	2	0.68	515	15269.573	0.001		1	0.73
303	15147.365	0.017		1	0.78	524	15330.705	-0.007		1	0.68
3 1 3	15156.643	0.011	0.003	2	0.71	533	15405.995	0.004		1	0.65
312	15169.659	-0.001	0.011	3	0.75	532	15406.433	0.001		1	0.67
322	15207.537	-0.004	0.007	2	0.69	633	15490.507	-0.003		1	0.64
321	15208.666	-0.046	0.004	3	0.67	707	15428.952	0.003		1	0.61
330	15281.213	0.008		1	0.66						

Note. Asterisks denote the energy levels excluded from the fitting. σ denotes the experimental uncertainties of the levels given in cm⁻¹. *N* is the number of lines sharing the same upper level. Δ is the difference between the experimental energy levels and the predictions of Ref. (7) (in cm⁻¹).

mental energy levels of the (600) state, including 11 energy levels derived from a single line (see Table 7). All but two of these energy levels were then fitted using six varied parameters. The rotational and centrifugal distortion parameters obtained (Table 8) are very close to those derived from PS's energy levels. Nonvaried parameters were fixed to the corresponding values of the (004) level (1), while the others were estimated from Ref. (7). The rms deviation of the fitting is 0.020 cm⁻¹.

The nearly constant positive shift of 0.7 cm⁻¹ of all the experimental energy levels relative to PS predictions is consistent with the 0.45 cm⁻¹ positive shift observed in Ref. (23) for the (500) state of HDO. Most of the assigned experimental lines correspond to the strongest calculated transitions. However, the experimental and calculated intensities (see Table 1) for the $6\nu_1$ band *A*-type transitions are, on average, three times larger than predicted by PS (7), while for all *B*-type transitions,

 TABLE 8

 Spectroscopic Constants of the (600) State of HDO (in cm⁻¹) (see text)

	From the experimental	From the data of
	energy levels	Ref. (7)
E_{v}	15065.73576(930)	15064.946
A	21.70062(540)	21.734
В	7.997392(850)	7.999
С	5.809895(500)	5.811
Δ_k	$6.394(550) \times 10^{-3}$	8.92×10^{-3}
Δ_{ik}	$1.370(110) \times 10^{-3}$	1.25×10^{-3}
Δ_{i}	4.2×10^{-4}	4.2×10^{-4}
δ_k	1.6×10^{-3}	1.6×10^{-3}
δ_i	1.5×10^{-4}	1.5×10^{-4}
H _k	3.4×10^{-5}	3.4×10^{-5}

PS's intensity estimations are less than 0.8×10^{-7} cm⁻²/atm, and so are not included in the resulting database.

4. CONCLUSION

The ICLAS absorption spectrum of the HDO molecule in the 14 980–15 350 cm⁻¹ region has been assigned to the [(014), (142), (0 12 0)] triad and modeled in the frame of the effective Hamiltonian approach. The results of the recent high-quality *ab initio* calculations of Partridge and Schwenke (7) were used as a guide to fix the vibrational states responsible for the strong perturbations observed in the bright $\nu_2 + 4\nu_3$ band. The identification of these states was also confirmed by the analysis of the intensity redistribution. An interesting example of intensity transfer from *A*- to *B*-type transitions induced by the coexistence of Fermi- and Coriolis-type interactions has been evidenced and successfully modeled.

An important feature revealed by the present analysis concerns the nature of the resonance coupling between the (014)bright state and the two highly excited bending states, (142)and $(0\ 12\ 0)$. This unexpected situation is attributed to a very high-order anharmonic coupling. An interpretation proposed in Refs. $(18,\ 20)$ is that strong centrifugal distortion associated with the bending vibrations may be responsible for such a resonance interaction. However, the origin of the resonances involving highly excited bending states is still far from being completely understood.

The necessity of taking into account several dark states to reproduce satisfactorily the line positions and intensities associated with one bright state indicates that, practically, we are at the border of the applicability of the effective Hamiltonian approach in its conventional form. The increase of the number of coupled states with energy may finally lead to the disappearance of good quantum numbers, except the J rotational quantum number, the highly excited rovibrational levels being characterized only by their energy values and symmetry.

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