# Experimental and *Ab Initio* Studies of the HDO Absorption Spectrum in the 13 165–13 500 cm<sup>-1</sup> Spectral Region

Olga Naumenko,\*<sup>,1</sup> Elena Bertseva,\* Alain Campargue,\* and David W. Schwenke†

\*Laboratoire de Spectrométrie Physique (associated with CNRS, UMR C5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France; and †NASA Ames Research Center, Moffett Field, California 94035-1000

E-mail: Alain.CAMPARGUE@ujf-grenoble.fr

Received January 12, 2000

The HDO absorption spectrum was recorded in the 13 165–13 500 cm<sup>-1</sup> spectral region by intracavity laser absorption spectroscopy. The spectrum (615 lines), dominated by the  $2\nu_2 + 3\nu_3$  and  $\nu_1 + 3\nu_3$  bands, was assigned and modeled leading to the derivation of 196 accurate energy levels of the (103) and (023) vibrational states. Finally, 150 of these levels were reproduced by an effective Hamiltonian involving two vibrational dark states interacting with the (023) and (103) bright states. The rms deviation achieved by variation of 28 parameters is  $0.05 \text{ cm}^{-1}$ , compared to an averaged experimental uncertainty of  $0.007 \text{ cm}^{-1}$ , indicating the limit of validity of the effective Hamiltonian approach for HDO at high-vibrational excitation. The predictions of previous *ab initio* calculations of the HDO spectrum (H. Partridge and D. Schwenke, *J. Chem. Phys.* **106**, 4618–4639 (1997)) were extensively used in the assignment process. The particular spectral region under consideration was used to test and discuss the improvements of new *ab initio* calculations recently performed on the basis of the same potential energy surface but with an improved dipole-moment surface. The improvements concern both the energy levels and the line intensities. In particular, the strong hybrid character of the  $\nu_1 + 3\nu_3$  band is very well accounted for by the new *ab initio* calculations. @ 2000 Academic Press

## 1. INTRODUCTION

In this paper, we continue our efforts started in Refs. (1, 2)aimed at the analysis of the near-infrared and visible absorption spectrum of HDO. The isotope substitution of one of the hydrogen atoms by deuterium strongly influences the intramolecular dynamics (3) and then changes the characteristics of the observed spectra. In Ref. (1), the  $4\nu_3$  absorption band centered at 13 853.631 cm<sup>-1</sup> was analyzed. (Note that we use in the present paper the traditional labeling of the stretching vibrations with  $\nu_1$  and  $\nu_3$  standing for the OD and OH stretching, respectively.) It was evidenced that up to  $v_3 = 5$ , the OH stretching states,  $(00v_3)$ , can be treated as isolated or at least slightly perturbed states. In Ref. (2), where the  $\nu_2 + 4\nu_3$ absorption band centered at 15 166.104 cm<sup>-1</sup> was investigated, strong resonance interactions between the (014), (142), and (012 0) vibrational states were revealed, leading to the observation of many absorption lines belonging to the  $\nu_1 + 4\nu_2 + 2\nu_3$ and the  $12\nu_2$  bands which borrow their intensities from the strong  $\nu_2 + 4\nu_3$  band lines partners. These unusual high-order resonances may result from strong centrifugal distortion effect induced by the excitation of the large-amplitude bending vibration (4). An interesting example of the intensity redistribution from A- to B-type transitions of the  $\nu_2 + 4\nu_3$  band due to

<sup>1</sup> On leave from the Institute of Atmospheric Optics, Russian Academy of Sciences, Tomsk, 634055, Russia.

the coexistence of both Fermi- and Coriolis-type interactions among the resonance triad was also evidenced (2).

In this work, the absorption spectrum of HDO in the 13 165–13 500 cm<sup>-1</sup> spectral region corresponding to the excitation of the (103) and (023) vibrational states is analyzed both experimentally and theoretically. This particular region will be used to test the improvements achieved recently by one of us (DS) in the prediction of the HDO spectrum from an *ab initio* potential energy and dipole momentum surfaces. The new calculations result in both more accurate line positions, due to better convergence of the rovibrational expansion, and more accurate line intensities, due to a better dipole-moment surface. This new level of accuracy is a great asset when analyzing the experimental spectrum.

## 2. EXPERIMENT

The experimental apparatus for ICLAS has been previously described (5). The technical details and a very recent review of the results obtained by ICLAS can be found in Ref. (6). 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  $H_2O$  and  $D_2O$  at a pressure of 14 Torr (18.4 hPa). This procedure led to a mixture of  $H_2O$ :HDO:D<sub>2</sub>O in a proportion close to 1:2:1. The spectra were obtained with a generation



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Wavenumbers, Intensities, and Rovibrational Assignments of the HDO Absorption Lines between 13 165 and 13 500 cm<sup>-1</sup>

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Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber	<b>a</b> .	(cm <sup>*</sup> /atm		$J K_a K_c$	$J K_a K_c$	State	Wavenumber	01-	(cm <sup>*</sup> /atm)	) L neook	$J K_a K_c$	$J K_a K_c$	State
(cm <sup>-</sup> )	Obs.		PS99*		716	-022	(cm )	1 ODS.		P899			102
13165.506	2.5E-6	4.2E-6	3.8E-6	615	/10	023	13189.254	1.2E-6	1.2E-6	7.3E-7	/16	817	103
13166.297	3./E-/	2.81:-/	1.8E-/	533	542	023	13189.689	1.0E-6	9.9E-/	/.9E-/	211	322	023
13166.824	6.8E-/	1.3E-6	5.1E-/	422	533	103	13189.835	2.0E-6	2.2E-0	1.8E-6	515	606	023
13166.824	6.8E-/	2./8,-/	1.2E-/	81/	830	023	13190.130	3.8E-7	4.1E-/	1.78-7	625	634	023
13166.922	5.4E-7	2.4E-/	4.6E-/	836	927	023	13190.245	2.6E-/	2.5E-/	1.2E-/	616	625	023
13167.212	2.8E-6	3.2E-6	2.5E-6	625	/26	023	13190.809	9.3E-7	7.9E-7	5.7E-7	615	726	103
13167.552	5.5E-7	1.9E-/	1.4E-/	431	440	023	13190.809	9.3E-7	2.0E-7	1.0E-/	919	928	103
13167.552	5.5E-7	2.8F-7	1.9E-7	532	541	023	13191.614	2.0E-7	2.0E-7	7.5E-8	707	716	023
13167.944	7.3E-7	5.0E-7	4.0E-7	542	643	023	13192.468	5.5E-7	6.0E-7	3.3E-7	717	716	023
13167.944	7.3E-7	5.2E-7	4.0E-7	541	642	023	13192.992	4.5E-7	3.2E-7	3.1E-7	735	826	023
13168.372	1.1E-6	1.2E-6	8.5E-7	413	524	023	13193.761	1.7E-6	1.6E-6	1.2E-6	633	734	103
13169.082	1.6E-6	2.1E-6	1.6E-6	606	717	023	13194.758	5.1E-7	4.6E-7	2.5E-7	524	533	023
13169.536	7.0E-7	4.9E-7	3.5E-7	753	854	103	13194.903	3.5E-7					
13169.536	7.0E-7	4.9E-7	3.5E-7	752	853	103	13195.077	1.7E-6	1.6E-6	1.2E-6	634	735	103
13169.663	6.9E-7	8.0E-7	5.2E-7	827	928	103	13195.473	2.8E-6	2.8E-6	2.4E-6	431	532	023
13169.986	3.2E-7	2.8E-7	1.3E-7	514	533	023	13195.885	2.7E-6	2.8E-6	2.4E-6	432	533	023
13170.363	5.0E-6	4.9E-6	5.4E-6	606	707	023	13196.204	6.7E-6	2.4E-6	1.2E-6	221	330	103
13170.681	4.8E-6	4.7E-6	5.2E-6	616	717	023	13196.204	6.7E-6	6.1E-6	5.7E-6	422	523	023
13171.953	2.0E-6	2.1E-6	1.6E-6	616	707	023	13196.751	8.5E-6	8.3E-6	8.2E-6	413	514	023
13171.953	2.0E-6	9.1E-7	7.2E-7	743	844	103	13198.621	2.7E-6	7.7E-7	6.3E-7	111	220	023
13172.144	7.6E-7	9.0E-7	7.2E-7	744	845	103	13198.621	2.7E-6	2.2E-6	1.8E-6	404	515	023
13175.141	6.0E-7	6.2E-7	3.0E-7	707	726	023	13199.329	8.7E-7	4.1E-7	1.9E-7	726	817	103
13175.343	6.3E-7	5.7E-7	2.7E-7	414	523	103	13199.531	1.3E-6	8.7E-7	5.2E-7	505	524	023
13175.940	1.5E-6	1.2E-6	8.8E-7	734	835	103	13199.682	6.7E-6	5.7E-6	5.5E-6	423	524	023
13175.940	1.5E-6	1.6E-7	6.4E-8	717	726	023	13199.682	6.7E-6	1.7E-6	1.0E-6	624	725	103
13177.290	6.4E-7						13201.544	1.5E-6	1.3E-6	9.8E-7	707	818	103
13177.847	1.2E-6	5.3E-7	3.2E-7	716	827	103	13201.580	1.6E-6	5.2E-7	4.1E-7	551	652	103
13177.847	1.2E-6	1.2E-6	8.4E-7	735	836	103	13201.580	1.6E-6	5.2E-7	4.1E-7	550	651	103
13178,130	2.3E-6	6.7E-7	5.5E-7	212	321	023	13202.130	1.3E-6	3.0E-7	1.9E-7	321	330	023
13178.130	2.3E-6	2.5E-6	2.0E-6	532	633	023	13202.130	1.3E-6	1 0E-6	6 1E-7	717	818	103
13178 483	1 1E-6	1.1E-6	8.4E-7	312	423	023	13202 231	2.0E-6	8 7E-7	7.0E-7	110	221	023
13178 660	1.0E-6	1.8E-6	8 2E-7	322	431	103	13202 231	2.0E-6	1.0E-6	6 1E-7	707	808	103
13179.006	2 3E-6	2.5E-6	2.0E-6	533	634	023	13202.231	1.0E-5	9.0E-6	1.0E-5	404	505	023
13179 248	4 3E-6	4 9E-6	4 3E-6	523	624	023	13202.510	1.0E-5	1.1E-6	8 5E-7	514	625	103
13181 152	6.4E-6	1.9E-6	8 2E-7	321	432	103	13202.009	1.7E-6	1.10-0	0.5E-7	717	808	103
13181 152	6.4E-6	63E-6	5.9E-6	514	615	023	13202.009	1.5E-6	1.5E-0	1.1E-7	028	077	023
13181 200	1.2E-6	1.3E-6	6 0E-7	725	826	103	13202.007	0.90 6	9 2E 6	0.4E 6	920 414	515	023
13182.025	1.2E-0	2157	1 3 5.7	661	767	103	13203.782	1 OF 6	0.5L-0	4 2E 7	212	122	1023
13182.925	4.705 7	2.15-7	1.36-7	660	761	103	13204.012	1.0E-0	7.0E-7	9.30-7	422	422	105
13182.925	4.70-7	4.65.6	1.3E=7	524	625	022	13204.314	0.3E-7	4.7E-7	1.75-1	422	431	1023
12182.300	4.9E-0	4.0E-0	4.3E-0	524	714	023	13205.201	2.0E-0	1.36-0	1.2E-0	542	643	103
13183.744	9.86-7	9.2E-7	3.1E-7	023	/10	1023	13205.201	2.05-0	1.3E-0	1.2E-0	541	642	103
13103.744	9.00-7	0.00.7	4.0E-7	010	919	103	13205.815	1.3E-0	1.3E-0	1.16-0	625	120	103
13184.148	8.0E-/	8.3E-/	0.2E-/	818	909	103	13205.926	9.4E-/	8.6E-/	5./E-/	524	615	023
13184.558	2.1E-0	2.3E-0	1.8E-0	505	010	023	13207.307	1.0E-0	1.012-0	J.1E-0	615	/10	103
13184.769	5.9E-/	( 0E 7	2 an a		~ + <b>^</b>	0.000	13207.454	9.4E-/	7.7E-7	4.9E-/	404	423	023
13185.588	1.8E-6	6.0E-7	3./E-/	441	542	023	13207.710	2.1E-6	2.1E-6	1.7E-6	414	505	023
13185.588	1.8E-6	6.0E-7	3./E-/	440	541	023	13208.387	5.7E-7	5.7E-7	2.9E-7	523	532	023
13185.588	1.8E-6	6.0E-7	4.5E-7	652	753	103	13208.629	2.4E-7	3.3E-7	1.9E-7	818	827	103
13185.588	1.8E-6	6.0E-7	4.5E-7	651	752	103	13208.877	2.5E-7					
13186.869	7.6E-6	6.9E-6	7.7E-6	505	606	023	13209.348	3.5E-7					
13187.541	7.4E-6	6.6E-6	7.4E-6	515	616	023	13211.393	2.0E-6	1.9E-6	1.6E-6	303	414	023
13187.966	1.1E-6	1.2E-6	7.7E-7	726	827	103	13211.523	2.1E-6	1.9E-6	1.5E-6	532	633	103
13188.593	1.3E-6	1.2E-6	1.0E-6	642	743	103	13212.385	4.4E-6	4.9E-7	3.4E-7	303	322	023
13188.700	1.6E-6	1.2E-6	1.0E-6	643	744	103	13212.385	4.4E-6	2.2E-6	2.0E-6	330	431	023
13188.700	1.6E-6	7.9E-7	4.3E-7	606	625	023	13212.385	4.4E-6	1.8E-6	1.5E-6	533	634	103

*Note.* The experimental, calculated, and predicted (*13*) intensities are given in cm<sup>-2</sup>/atm at 296 K and correspond to pure HDO. The total calculated and experimental line intensities are normalized (see text) to the total intensity predicted in Ref. (*13*). Lines blended by  $H_2^{16}$ O are marked by "b." In case of doublets, the same experimental intensity is given for the two components while the calculated intensities from the EH or from Ref. (*13*) correspond to each component.

<sup>a</sup> Intensity predictions of the effective Hamiltonian model.

<sup>b</sup> Intensity predictions of Ref. (13).

time of 100  $\mu$ s corresponding to an equivalent absorption path length of 15 km. A Styryl 8 dye solution was used to record the spectrum between 13 165 and 13 500 cm<sup>-1</sup>. The relatively strong  $b^1\Sigma_g^+(0) \leftarrow X^3\Sigma_g^-(0)$  absorption band of atmospheric oxygen present in the laser cavity prevents the measurement of HDO lines below 13 165  $cm^{-1}$ .

The spectral resolution of the high-resolution grating spectrograph dispersing the laser spectrum is about  $0.025 \text{ cm}^{-1}$ ,

Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber		(cm <sup>-2</sup> /atm	)	J Ka Ke	J K <sub>a</sub> K <sub>c</sub>	State	Wavenumber		(cm <sup>-2</sup> /atm)	)	$J K_a K_c$	JK <sub>a</sub> K <sub>c</sub>	State
(cm <sup>-1</sup> )	Obs.	Calc <sup>a</sup>	PS99 <sup>b</sup>				(cm <sup>-1</sup> )	Obs.	Calc. <sup>a</sup>	PS99 <sup>b</sup>			
13212.548	1.0E-5	9.4E-6	9.7E-6	312	413	023	13241.521	7.2E-7	8.2E-7	4.9E-7	404	413	023
13212.548	1.0E-5	2.2E-6	2.0E-6	331	432	023	13241.789	3.3E-7					
13213.367	6.3E-6	6.1E-6	6.3E-6	321	422	023	13242.638	2.3E-6	2.1E-6	1.6E-6	413	514	103
13214.241	1.6E-6	1.4E-6	1.2E-6	413	524	103	13242.973	5.7E-7	3.0E-7	2.8E-7	533	624	023
13215.352	4.5E-7	3.7E-7	1.4E-7	817	826	023	13243.567	9.4E-7	8.8E-7	5.1E-7	321	330	103
13215.666	5.9E-6	5.9E-6	5.8E-6	322	423	023	13243.878	1.3E-6	1.1E-6	9.8E-7	212	303	023
13216.475	4.3E-7	3.1E-7	1.1E-7	927	936	023	13244.225	3.7E-7	9.1E-8	6.4E-8	734	827	023
13216.886	3.7E-7	5.6E-7	2.3E-7	725	734	023	13244.797	1.0E-6	1.1E-6	6.8E-7	422	431	103
13217.622	1.1E-5	1.0E-5	1.2E-5	303	404	023	13244.982	7.8E-6	6.2E-6	7.0E-6	110	211	023
13218.061	2.0E-6	2.0E-6	1.3E-6	523	624	103	13245.667	6.7E-7	6.0E-7	3.2E-7	524	615	103
13218.676	2.1E-6	1.8E-6	1.4E-6	606	717	103	13246.355	1.7E-6	1.3E-6	1.2E-6	330	431	103
13218.676	2.1E-6	3.4E-7	3.0E-7	634	725	023	13246.492	1.6E-6	1.3E-6	1.2E-6	331	432	103
13219.521	1.0E-5	9.2E-6	1.1E-5	313	414	023	13246.682	1.9E-6	1.6E-6	1.4E-6	414	413	023
13219 846	1.5E-6	1.4E-6	8.8E-7	616	717	103	13247.203	1.0E-6	1.1E-6	6.6E-7	523	532	103
13219 968	14E-6	1.4E-6	8 8E-7	606	707	103	13247 510	1.0E-5	8 7E-6	1.0E-5	101	202	023
13220 523	4 7E-7	4 4E-7	2 9E-7	313	322	023	13248 545	7.4E-7	6.6E-7	54E-7	000	111	023
13221.010	6 6E-7	5.5E-7	2.9E-7	726	735	103	13248 988	1 4E-6	1.9E-6	1 3E-6	111	220	103
13221.010	2.0E-6	1.7E-6	13E-6	616	707	103	13249 198	3.2E-7	4.6E-8	3.6E-8	808	725	023
13221.134	2.0E-0	1.05-6	9.8E-7	441	542	103	13249.198	2.7E-6	2.6E-6	2.2E-6	404	515	103
13221.004	2.76-0	1.0E-6	0.85.7	440	5 4 1	103	13249.404	73E.6	6.0E-6	716-6	111	212	023
13221.094	1 9E-7	5.4E-7	2.6E-7	625	716	103	13249.739	7.3E-6	4 4E-7	3 1E-7	322	413	023
13222.307	4.75.7	3.4E-7	2.0L-7	877	876	023	13250 111	8 7E-7	8 5E.7	5.5E 7	624	633	103
13222.801	1.0E_6	10E-6	13E-6	524	625	103	13251 307	1.1E-6	1.0E-6	6.0E-7	303	312	023
12222.510	1.75.6	1.5E.6	1.30-0	202	212	023	13251.307	1.10-0	91E 9	9 2E 9	643	774	023
13223.427	4 OF 7	5 45 7	2 20 7	717	776	102	13251.307	1.10-0	0.1L-0	7 OF 7	515	524	1023
13224.912	0.7E-/	1.00 6	1456	514	615	103	13251.924	1.20-0	1.16-0	1.75-7	622	724	022
12225.055	1704	1.75.6	1.5E.6	212	404	022	13251.924	1.20-0	1.5L-7	1.20-7	110	221	1023
13225.755	1.76-0	1.7E-0	1.55-0	212	404	1023	13232.218	7 2 5 7	5 7E 7	1.5E-0 4 IE 7	725	724	103
13220.113	5.90 7	5.5E 7	2.05.7	505	514	022	13252.402	1.20-7 4.6E 7	2467	9.10-7	915	014	022
13227.931	5 912 7	5.5E=7	2.76-7	714	714	023	13232.767	9.00-7	3.0E-7	9.0E-0	404	505	1023
13227.331	5.0D=7	6 95 7	4757	172	514	023	12252.417	2.30-0	2.01-0	1.40-0	917	014	105
12220.111	0.0L-7	150.6	4.7E=7	423	221	102.5	13253.417	2.56-0	3.0E-/	2.2E-/	414	515	103
12220.300	0.4L-/	0.05.6	0.7E 6	212	212	022	132554.000	1 25 6	1 75 4	0 SE 7	414	614	022
12220.022	0.55-0	9.0E-0	9.7E-0	421	512	1023	13254.090	1.26-0	1.2E-0	0.JE-/	221	422	1025
13229.134	2.10-0	1.05-0	1.05-0	431	552	103	13234.700	1.0E-0	1.96-0	1.36-0	321	422	105
12229.341	2.0E-0	1.0E-0	1.0E-0	432	222	103	13236.430	3.9E-7	0.3E-/	2.3E-/	/44	743	023
12220.435	J.JE-0	4.4C-0	J.JE-0	515	521	023	13230.334	2.9E-/	1.1E-0	1.0E-0	222	133	1023
12221 522	1.06-0	1.1E-0 4.4E-6	0.0E-/	221	214	023	12257.300	1.96-0	1.96-0	1.00-6	322	423	103
13231.333	4.2E-0	4.4E-0	4.4E-0	221	322	023	13237.394	2.2E-0	2.3E-0	1.96-0	414	202	103
13232.501	9.46-0	1.12-5	1.2E-3	202	303	1023	13257.033	9.8E-7	1.1E-0	1.7E=7	202	211	023
13234.300	0.4E+/	1.1E-0	0.0E-/	324	233	103	13259.302	1./E-/	9.8E-/	5.3E-/	043	042	023
13234.810	8.1E-0	8./E-0	1.0E-5	212	313	023	13259.444	2.4E-0	2.3E-0	2.4E-0	313	312	023
13235.550	1.1E-0	1.1E-0	9.0E-7	101	212	023	13259.551	8.1E-/	9.1E-/	5.3E-/	642	643	023
13235.811	5.8E-/	4.0E-/	3.1E-/	211	220	023	13260.169	2.1E-0	2.1E-6	1.6E-6	312	413	103
13236.484	1.8E-6	2.1E-6	1.5E-6	422	523	103	13260.627	7./E-/	8.6E-/	6.2E-/	606	615	103
13236.957	1./E-0	1.7E-6	1.1E-6	515	616	103	13261.191	8.0E-/	8.1E-/	0.2E-/	101	110	023
13236.994	1.8E-0	1./E-6	1.2E-6	505	606	103	13261.626	1.8E-6	1.5E-6	1.1E-0	542	541	023
13237.684	4.3E-7	1.2E-6	1.5E-/	652	651	023	13261.660	2.0E-6	5.0E-7	4.5E-/	111	202	023
13237.684	4.3E-/	1.2E-6	1.5E-/	051	652	023	13261.660	2.0E-6	1.5E-6	1.1E-6	541	542	023
13238.474	8.6E-7	8.0E-7	5.1E-7	312	321	023	13262.303	1.4E-6	1.4E-6	1.1E-6	414	423	103
13238.611	1.1E-6	1.2E-6	6.6E-7	423	432	103	13262.856	5.8E-6	5.0E-6	6.0E-6	000	101	023
13238.700	2.1E-6	1.9E-6	1.6E-6	211	322	103	13263.046	2.6E-6	2.7E-6	2.4E-6	303	414	103
13239.254	1.9E-6	2.2E-6	1.7E-6	515	606	103	13263.493	4.4E-6	3.5E-6	2.2E-6	441	440	023
13239.418	7.6E-7	8.1E-7	5.3E-7	616	625	103	13263.493	4.4E-6	3.6E-6	2.2E-6	440	441	023
13239.675	7.7E-7	1.1E-6	5.5E-7	514	523	023	13264.119	7.8E-7	7.9E-7	3.8E-7	735	734	023
13240.055	6.8E-7	6.6E-7	4.9E-7	726	725	023	13264.447	2.2E-6	2.1E-6	2.0E-6	524	523	023
13240.168	7.9E-7	1.0E-6	6.0E-7	413	422	023	13265.576	4.2E-7	2.2E-7	2.2E-7	432	523	023
13240.454	2.1E-6	2.0E-6	1.5E-6	423	524	103	13265.777	3.6E-7					
13240.844	6.4E-7	5.3E-7	3.5E-7	707	716	103	13267.439	4.0E-7	1.7E-7	1.6E-7	404	321	023
13241.321	8.6E-7	8.8E-7	5.1E-7	322	331	103	13267.702	7.0E-7	7.3E-7	4.2E-7	716	725	103

**TABLE 1**—Continued

which is less than the Doppler broadening (0.038 cm<sup>-1</sup> FWHM). The wavenumber calibration procedure is described in Refs. (*1*, *2*, and *6*). It requires the use of two reference lines for each elementary ICLAS spectrum of about 15 cm<sup>-1</sup> width. Lines due to H<sub>2</sub>O (7) appearing superimposed on the HDO spectrum were used as references in the 13 400–13 500 cm<sup>-1</sup> spectral region. However, the H<sub>2</sub>O spectrum becomes too sparse below 13 400 cm<sup>-1</sup>. In consequence, in the 13 165–13 400 cm<sup>-1</sup> region, we were obliged to use as reference lines a few HDO lines calculated using ground state combination

differences (GSCD) and rotationally assigned lines measured in the 13 400–13 500  $\text{cm}^{-1}$  region.

We estimate our wavenumber calibration to be accurate to within 0.01 cm<sup>-1</sup> as will be confirmed by the uncertainty obtained for the energy levels determined from several transitions. After suppression of the  $H_2O$  lines, the final data set corresponds to 615 lines listed in Table 1 and plotted in Fig. 1a.

The relative intensities of the lines were roughly estimated from the peak depth of each line. In spite of its limited accuracy, this information will prove to be highly valuable in

**TABLE 1**—Continued

01 11		Interaiter		Linnor	Louvan	Vib	Observed	I	Intensity		Unner	Lower	Vib
Wasserved		(cm <sup>-2</sup> /otm)				VID. State	Wavenumber		(cm <sup>-2</sup> /stm)				State
(am <sup>-1</sup> )	Ohe	(chi /aun)	PS00b	JAGAC	JKaKc	State	(cm <sup>-1</sup> )	Obs	Calc <sup>a</sup>	PS99 <sup>b</sup>	JAANC	J Ka Kc	State
12268.070	2 2 5 7	Calc	1397				13293 455	3 0F-7	cuit	10,,,			
13268 204	4.1E-7						13293 689	5.0E (	5 2E-6	64E-6	1.0.1	000	023
13268 860	4.1L-7 5.5E-7	5 7E-7	3.2F-7	423	514	103	13293.831	4 4E-7	5.2E-7	4 0E-7	853	854	103
12268.800	1956	2.6E-6	11E-6	212	211	023	13294.068	2.5E-6	1.6E-6	14E-6	212	303	103
12269.034	1.05.6	2.0E-6	1.5E-6	303	404	103	13294.068	2.5E-6	1.0E-6	8.8E-7	753	752	103
13209.270	1.90-0	2.01-0	1.30-0	212	404	103	13294.068	2.5E-6	1.0E-6	8 QE_7	752	753	103
12270 471	1.90-6	1057	13E-7	221	312	023	13294.000	3 1E-6	2 0E-6	1.8E-6	652	651	103
13270.471	1.90-6	1.90-7	1.3E-6	313	322	103	13294.441	3 1E-6	2.0E-6	1.8E-6	651	652	103
13270.471	2704	2.5E.6	2706	422	122	023	13204 801	4.2E-6	3.6E-6	3.2E-6	551	550	103
13271.312	3.7E-0	2.00 6	3.7E-0	522	527	023	13294.801	4.2E-0	3.6E-6	3.2E-6	550	551	103
13272.120	1.50.6	1.70-0	110 6	220	321	103	13204.001	7.6E-7	1 1E-6	0 3E-7	110	211	103
12272.000	5 1E 6	1.3E-6	1.1E-6	220	327	103	13295 137	1.5E-6	1.1E-0	2 1E-6	312	313	023
13273.001	5.1E-0	1.3E-0	1.1E-0	432	121	023	13295.157	7.76-7	0.5E-7	2.1E-0 8.1E-7	110	101	023
12273.001	2.1E-0	J.0E-0	4.2E-0	432	522	023	13295.051	/ 0E-7	4.6E-7	1 2E-7	845	844	103
13274.130	2.3E-0	2.0E-0	4 25 6	121	133	023	13295.629	9.0E-7	9.0L-7	9.0E-7	744	743	103
13274.400	4.4C-0	5.0E-0	4.2E-0	431	432	023	13297.094	4 2E 7	5 2E 7	4 AE 7	725	743	103
13274.802	1.5E-0	1.JE-0	7.0E-0	221	220	023	13297.495	4.JE#7	9 OF 7	7 25 7	621	625	023
13274.981	0.9E-0	0.7E-0	7.0E-0	220	221	023	13297.701	176.6	1756	1.20-7	612	612	1023
13275.042	0.JE-0	0./E-0	7.0E-0 9.2E C	111	110	023	13298.030	1.75-0	0.05 7	9 OF 7	712	744	103
13275.382	8.0E-0	7.1E-0	0.3E-0	212	404	102	13298.030	1.76-0	9.0E=7	1756	643	643	103
13275.630	7.20-0	2.2E-0	1.0E-0	2 2 2 2	221	022	13290.294	1.4E-0	1.76-0	1.70-0	211	202	023
13275.030	7.2E-0	0.1E-0	0.7E-0	322	212	1025	13290.001	4.50-0	2.05.6	2.200	542	511	1023
13275.807	2.96-0	2.JE-0	1./E-0	202	221	103	13290.001	4.50-0	3.0E-0	3.20-0	541	547	103
13276.443	2.3E-0	1.1E-0	2.1E-0	212	221	002	13290.001	4.JE-0	5.0E-0	5.4E-0	441	142	103
13277.281	1.7E-7	0.9E-/	4.35-7	734	212	1023	13299.010	0.4E-0	5.2E-0	J.0E-0	441	440	103
13277.636	1.2E-5	1.8E-0	1.4E-0	211	312	103	13299.010	0.46-0	J.2E-0	0.0E-0	440	441	103
13277.636	1.2E-5	1.1E-5	1.2E-5	221	514	1023	13300.140	9.76-7	1.1E-0	9.2E-/	101	212	103
13278.099	1.3E-0	1.3E-0	1.0E-0	202	221	002	13300.434	1.2E-0 2.1E-7	1.4E-0	1.26-0	101	202	105
132/8.558	9.5E-0	1.1E-3	1.0E-3	220	221	023	13300.700	3.1E-7	1556	1 45 6	0.0.0	1 1 1	102
13278.804	3.8E-/	1.4E-7	1./E-/	321	414	1023	13301.801	1.3E-0	1.3E-0	1.4E-0	600	(1)	103
132/9.19/	2.2E-/	1.4E-/	9.4E-8	937	930	103	13302.3250	1.46-0	9.06-/	8.8E-/	034	033	103
13279.389	3.1E-/	2 OF (	6 OF (	2.2.1		022	13302.902	2.1E-0	2.0E-0	2.2E-0	303	312	105
132/9.810	6.0E-6	5.8E-6	5.9E-6	321	322	023	13303.810	3.0E-/	1 45 6	1157	212	202	022
13281.353	7.6E-6	0./E-0	8.1E-0	110	111	023	13304.198	1.0E-0	1.4E-0	1.1E-0	512	505	1023
13283.166	3.3E-6	3.1E-6	3.1E-6	422	423	023	13304.198	1.05-0	5./E-/	4.4E-/	524	523	103
13283.553	1.3E-6	1.8E-6	1.2E-6	514	223	103	13305.406	7.8E-0	0./E-0	8.3E-0	212	414	023
13284.862	1.8E-6	1.8E-6	1.1E-6	202	303	103	13305.620	1.5E-0	1.1E-0	1.2E-0	413	414	023
13284.975	1.4E-6	1.8E-6	1.2E-6	212	313	105	13307.522	4.8E-0	2.8E-0	2.8E-0	432	431	103
13285.334	2.5E-/	215 (	1.25.6		4.2.2	107	13307.522	4.8E-0	1.0E-0	1.01-0	532	333	103
13286.061	2.1E-6	2.1E-6	1.3E-6	413	422	103	13307.887	7.5E-/	3.4E-/	4.4E-/	4 7 1	422	1023
13286.090	2.0E-6	2.0E-6	1.1E-0	312	321	103	13308.049	3.3E-0	2.8E-0	2.8E-0	431	432	103
13286.297	5.5E-/	3.8E-/	2.0E-7	8/2	8/1	103	13308.300	1.0E-5	9.3E-0	1.2E-5	202	101	1023
13286.297	5.5E-/	3.8E-/	2.0E-7	8/1	8/2	103	13308.932	5.7E-0	4.7E-0	4.7E-0	331	330	103
13286.385	7.8E-7	7.9E-7	4.0E-7	771	770	103	13308.998	5.0E-0	4.7E-0	4.76-0	330	212	103
13286.385	7.8E-7	7.9E-7	4.0E-/	770	771	103	13309.405	6.1E-/	3./E-/	2.2E-/	313	312	103
13286.621	1.2E-7	6.5E-8	3.0E-8	312	221	023	13309.652	4./E-/	4.1E-/	2.1E-/	303	212	023
13286.953	3.3E-6	3.2E-6	3.8E-6	211	212	023	13310.019	2.9E-0	2.8E-0	1.9E-0	202	211	103
13288.517	2.1E-6	2.1E-6	1.9E-6	101	212	103	13310.848	7.2E-7	4.9E-/	4.5E-/	/ 3 4	135	103
13289.178	1.4E-6	1.6E-6	1.6E-6	523	524	023	13311.132	5.4E-7	1.9E-6		8/2	914	004
13289.898	4.1E-7	2.8E-7	2.2E-7	836	835	103	13311.132	5.4E-7	1.9E-6		871	924	004
13290.983	8.2E-7	4.7E-7	3.2E-7	863	862	103	13311.254	5.4E-7					
13290.983	8.2E-7	4.7E-7	3.2E-7	862	863	103	13311.847	1.1E-6	1.2E-6	9.5E-7	413	404	023
13291.065	1.6E-6	9.7E-7	6.8E-7	762	761	103	13312.099	1.1E-6	8.3E-7	/.8E-7	111	202	103
13291.065	1.6E-6	9.7E-7	6.8E-7	761	762	103	13312.256	1.1E-6	9.5E-7	8.0E-7	423	422	103
13291.279	2.6E-6	1.9E-6	1.3E-6	661	660	103	13312.584	7.2E-6	0.3E-6	/.9E-6	211	110	023
13291.279	2.6E-6	1.9E-6	1.3E-6	660	661	103	13312.796	0.8E-7	2.2E-7	1.5E-7	221	312	103
13292.004	2.1E-7					0.55	13314.138	2.4E-6	2.2E-6	2.0E-6	101	110	103
13292.170	2.4E-7	4.4E-8	4.6E-8	440	533	023	13314.580	5.0E-7					
13292.379	1.4E-6	2.0E-6	1.6E-6	404	413	103	13314.875	6.3E-7			0.0.0	101	100
13292.731	2.8E-7	3.6E-7	2.3E-7	625	624	103	13316.106	1.2E-6	7.7E-7	6.5E-7	000	101	103

the spectral assignment process. This method leads to relatively strong deviations both for the stronger and the weaker lines. These 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.

# 3. THEORETICAL ANALYSIS AND RESULTS

The initial approximation for the rotational and centrifugal distortion constants of the (103) and (023) states was derived

from *ab initio* predictions by Partridge and Schwenke (8). Transformed dipole-moment parameters were also estimated from the comparison of the calculated and observed line intensities and used as input data for the program exploited for an automatic spectra identification (9). As the experimental energy levels were derived from the experimental data, spectroscopic constants were refined from the fitting to observed line positions and intensities, in the frame of the effective Hamiltonian (EH) method providing more accurate extrapolations. The predictions of Ref. (8) were also used as a guide in the identification process. Finally 557 absorption lines were as-

Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber		(cm <sup>-2</sup> /atm)	•	J Ka Ka	$J K_{a} K_{c}$	State	Wavenumber		(cm <sup>-2</sup> /atm)	)	$J K_{\alpha} K_{c}$	J Ka Kc	State
(cm <sup>-1</sup> )	Obs.	Calc.ª	PS99 <sup>b</sup>				(cm <sup>-1</sup> )	Obs.	Calc. <sup>a</sup>	PS99 <sup>b</sup>			
13316.195	7.8E-7	2.5E-7	2.1E-7	835	836	103	13340.129	4.7E-7	4.1E-7	2.4E-7	927	918	023
13316.588	6.7E-7	L.8E-7	2.3E-7	313	220	103	13342.579	6.2E-7	6.6E-7	5.9E-7	524	515	023
13317.254	2.7E-6	1.6E-6	1.4E-6	322	321	103	13342.760	5.8E-7	4.1E-7	3.6E-7	312	313	103
13317 254	2 7E-6	1.6E-6	1 3E-6	422	413	023	13343.017	1.1E-5	1.1E-5	1.5E-5	505	404	023
13317 571	1.5E-6	1.6E-6	1.2E-6	523	514	023	13343.150	6.7E-6	6.4E-6	7.6E-6	422	321	023
13317 783	1.0E-5	1.0E-5	1 3E-5	313	212	023	13343 808	1.0E-6	1 1E-6	1 0E-6	532	523	023
13318 745	1.5E-6	1.2E-6	1.2E-6	321	312	023	13344 291	3.6E-7	3 1E-8	1 8E-8	10.2.8	1029	023
13319 188	8 5E-7	5 9E-7	3 1E-7	212	211	103	13344.378	3.8E-7					
13319 693	7.4E-7	6 3E-7	4 5E-7	212	101	023	13344.874	5.2E-7	4.2E-7	3.3E-7	716	707	023
13319 971	3.2E-6	2 8E-6	2.5E-6	221	220	103	13345.543	8.8E-6	9.9E-6	1.2E-5	413	312	023
13320 129	1.5E-6	1.4E-6	9.8E-7	624	615	023	13345.625	1.7E-6	2.0E-6	2.1E-6	110	101	103
13320.788	3.1E-6	2.8E-6	2.5E-6	220	221	103	13345.880	3.7E-7					
13321 238	2 0E-6	1.6E-6	1.4E-6	321	322	103	13346.117	3.9E-7	2.6E-7	2.6E-7	624	533	103
13321 298	1.6E-6	6.9E-7	8.6E-7	220	211	023	13346.392	9.7E-7	9.0E-7	6.6E-7	202	111	103
13321.610	1.2E-5	1.2E-5	1.5E-5	303	202	023	13346.631	1.0E-6	7.6E-7	6.7E-7	101	000	103
13321.847	8 1E-7	2 3E-7	1.5E-7	625	532	103	13346 904	4 3E-7					
13322 281	6.9E-7	2.5E-7	2 5E-7	414	321	103	13347 911	2.7E-6	2.6E-6	2.7E-6	211	2.0.2	103
13323 435	1.0E-6	9.2E-7	7.8E-7	422	423	103	13348.056	1 1E-6	9.0E-7	94E-7	431	422	023
13323 781	5 1E-6	4 8F-6	5.8E-6	322	221	023	13349.012	6.6E-7	5 1E-7	4 0E-7	625	616	023
13324 095	4 7E-7	4.8E-7	1.8E-7	404	313	023	13349 267	8 3E-6	9 5E-6	1 2E-5	616	515	023
13324 943	8 8F-7	1 1E-6	6.9E-7	725	716	023	13351.040	3.0E-6	3.0E-6	3.0E-6	533	432	023
13325 768	1.4E-6	1.2E-6	1.0E-6	111	110	103	13351.397	6.3E-6	6.7E-6	8.2E-6	524	423	023
13325 933	4.9E-6	4 7E-6	5 5E-6	321	220	023	13351 583	8 7E-6	9.6E-6	1.2E-5	606	505	023
13327 975	5.5E-7	54E-7	4 2E-7	523	524	103	13351 828	2.4E-6	2 5E-6	2.6E-6	312	303	103
13328 273	2.0E-7	19E-7	1.2E-7	726	633	103	13352.128	2.9E-6	3.0E-6	3.0E-6	532	431	023
13328 500	3 9E-7	3 5E-7	3 IE-7	936	927	023	13352.515	1.1E-6	5.5E-7	2.6E-7	413	322	103
13328 787	4 3E-7	5 2E-7	4 6E-7	221	212	023	13352.515	1.1E-6	8.3E-7	9.0E-7	432	423	023
13329 277	1.1E-5	1.2E-5	1.5E-5	414	313	023	13352.628	8.5E-7	5.6E-7	6.3E-7	331	322	023
13329 346	9.9E-6	93E-6	1.2E-5	312	211	023	13352 891	1.0E-6	9.0E-7	9 1E-7	533	524	023
13329 751	5 3E-7	6 3E-7	3 7E-7	313	202	023	13353 023	6.8E-7	6 9E-7	5 5E-7	643	542	023
13329 922	3 5E-7	0.510	0.70 .	5.5	202	020	13353 183	7.2E-7	3 8E-7	3 3E-8	616	505	023
13330 255	1.8E-7						13353 183	7.2E-7	64E-7	5.5E-7	642	541	023
13330.458	5.8E-7						13353 907	9 3E-7	8 2E-7	7 9E-7	634	625	023
13330 813	4 7E-7	4.1E-7	3.7E-7	615	616	023	13354.406	9.3E-7	7.2E-7	7.3E-7	221	110	023
13330.813	4 7E-7	1 3E-7	7.0E-8	827	734	103	13355 558	1.5E-6	1 1E-6	1.2E-6	212	111	103
13331 345	1 4E-6	1 2E-6	1.0E-6	110	111	103	13355.652	1.0E-6	6.5E-7	6.1E-7	735	72.6	023
13331 345	1.4E-6	9.2E-8	1.4E-8	725	634	023	13355.926	6.0E-7	2.6E-7	2.1E-7	817	808	023
13331 830	4 7E-7	7.0E-7	4.3E-7	826	817	023	13356.372	1.6E-6	1.8E-6	1.5E-6	523	514	103
13332 326	6 4E-7	7 3E-7	6.5E-7	322	313	023	13357.271	1.2E-6	1.2E-6	1.0E-6	624	615	103
13333 180	1 3E-5	1.2E-5	1.6E-5	404	303	023	13357.495	1.8E-6	2.0E-6	L8E-6	422	413	103
13334 074	9.4E-7	1.0E-6	7.4E-7	734	725	023	13357.747	8.4E-6	1.9E-6	2.0E-6	413	404	103
13334 542	4.6E-7						13357.747	8.4E-6	7.4E-6	9.4E-6	717	616	023
13334 704	5.4E-7						13358.259	1.7E-6	1.4E-6	1.5E-6	111	000	103
13334 908	4 4E-7	3 4E-7	2.1E-7	624	625	103	13358.613	9.3E-7	4.4E-7	4.4E-7	836	827	023
13335 516	3 3E-7	6 2E-8	3.0E-8	1037	10.3.8	103	13358.710	9.2E-7	3.4E-7	4.5E-7	743	734	023
13335.830	6.9E-7	0.220	0.000				13359.240	7.1E-6	7.4E-6	9.4E-6	707	606	023
13335 971	6.3E-7	6.2E-7	5.6E-7	211	212	103	13359.782	4.6E-7	2.8E-7	1.4E-7	937	928	023
13336 150	3 9E-7						13360.167	1.6E-6	1.8E-6	1.6E-6	321	312	103
13336 541	2.2E-6	2 4E-6	2.4E-6	432	331	023	13360.457	6.3E-7	7.1E-7	5.3E-7	725	716	103
13336 846	2.3E-6	2.3E-6	2.4E-6	431	330	023	13360.686	9.0E-6	1.4E-6	9.5E-7	202	101	103
13336 967	6.8E-7	7.5E-7	6.8E-7	423	414	023	13360.686	9.0E-6	8.8E-6	1.1E-5	514	413	023
13337 956	6 5E-6	6.7E-6	8.1E-6	423	322	023	13360.969	5.7E-6	6.3E-6	7.4E-6	523	422	023
13338 326	4 6E-7	5.8E-7	2.4E-7	414	303	023	13361.297	1.8E-6	1.7E-6	1.7E-6	303	212	103
13338 554	4 3E-7	2.01.7				020	13361.595	1.4E-6	1.2E-6	9.3E-7	211	110	103
3338 817h	1 3E-6	1.1E-6	9.3E-7	633	624	023	13362.719	1.1E-6	2.3E-7	2.1E-7	827	818	023
13339 563	1 1E-6	4 7E-7	4.9E-7	542	441	023	13362.979	6.0E-7		8.7e-7	633	524	151
13339 563	1 1E-6	4 9E-7	4 9E-7	541	440	023	13363.154	8.8E-7	2.4E-7	3.0E-8	716	625	023
13339 768	9.9E-6	1 1E-5	1.4E-5	515	414	023	13363.154	8.8E-7	3.7E-7	4.4E-7	744	735	023
1000	7.70.0			212		025	100001101						025

**TABLE 1**—Continued

signed to the  $\nu_1 + 3\nu_3$  and the  $2\nu_2 + 3\nu_3$  bands transitions leaving 51 weak lines (7%) unassigned (see Table 1). One hundred ninety-seven experimental energy levels, listed in Table 2, were derived from the observed frequencies by adding the lower state energy obtained from Ref. (10). Table 2 includes the number of lines used in the determination of each level, the corresponding experimental uncertainties, and the difference between the experimental and predicted (8) energy levels. For small J values, these differences are on the order of 0.08 and 0.13 cm<sup>-1</sup> for the  $\nu_1 + 3\nu_3$  and  $2\nu_2 + 3\nu_3$  band, respectively, but increase up to 2.6 cm<sup>-1</sup> for J = 12, 13 levels.

Since the highly excited vibrational states of HDO are sub-

ject to strong centrifugal distortion effect, the effective rotational Hamiltonian in the Pade–Borel approximation (11–12) was used in the fitting of the experimental energy levels. (Note that the spectroscopic constants of this Hamiltonian have the same meaning as those used in the traditional Watson Hamiltonian.) In contrast with the H<sub>2</sub><sup>16</sup>O molecule, which has distinct polyad structure, no clear resonance polyad scheme was evidenced in HDO. It is then difficult to fix *a priori* the possible resonance, especially at a high degree of vibrational excitation. In our case, it was clear that the energy levels of both (103) and (023) states are strongly perturbed for  $J \ge 4$ . The identification of the perturbers on the basis of the predictions of Ref. (8)

**TABLE 1**—Continued

Observed		Intensity		Unner	Lower	Vih	Observed		Intensity		Unner	Lower	Vih
Wavenumber		(cm <sup>-2</sup> /atm	)	$J K_a K_c$	$J K_a K_c$	State	Wavenumber		(cm <sup>-2</sup> /atm)	)	J Ka Kc	J Ka Ku	State
(cm <sup>-1</sup> )	Obs.	Calc. <sup>a</sup>	PS99 <sup>b</sup>				(cm <sup>-1</sup> )	Obs.	Calca	PS99 <sup>b</sup>			
13363.527	1.2E-6	1.1E-6	1.0E-6	220	211	103	13382.871	1.2E-6	4.3E-8	9.0E-7	11 111	$10\ 010$	023
13363.784	8.0E-7	3.4E-7	5.7E-7	642	633	023	13383.410	2.1E-6	2.0E-6	1.9E-6	422	321	103
13364.000	5.3E-6	5.7E-6	6.1E-6	625	524	023	13384.027	2.3E-6	1.8E-6	1.7E-6	404	303	103
13364.726	6.0E-7	3.0E-7	1.3E-7	835	826	103	13384.399	2.5E-6	2.1E-6	2.2E-6	533	432	103
13365.107	2.6E-6	2.7E-6	2.6E-6	634	533	023	13384.519	1.9E-6	1.9E-6	1.9E-6	734	633	023
13365.292	5.1E-6	5.1E-6	6.7E-6	818	717	023	13384.649	6.0E-7	4.2E-7	4.2E-7	716	707	103
13365.405	1.1E-6	1.3E-6	1.3E-6	322	221	103	13384.956	2.4E-7	6.2E-7	3.2E-7	330	321	103
13365.610	1.2E-6	1.3E-6	1.4E-6	514	505	103	13385.513	9.6E-6	2.1E-6	2.2E-6	532	431	103
13365.752	5.6E-7	3.6E-7	5.6E-7	643	634	023	13385.513	9.6E-6	4.8E-6	5.9E-6	/10	615	023
13366.165	5.5E-6	1.1E-/	4.46-7	744	043	023	13385.513	9.0E-0	2.8E-0	3.4E-0	827	120	1023
13300.103	5.5E-0 4.0E 7	4.9E-0	0.7E-0	2 2 2 2	211	023	13380.148	4.46-7	3.0L-7	4.00-7	432	425	103
13300.323	4 26 7	63E7	J.0E-7	743	642	023	13386.246	4.4E-7	3.4L-7 7.5E-7	3.5E-7	524	524	103
13366 854	6.0E-7	2.5E-7	4.4E-7	725	634	103	13386 589	3.6E-7	6 1E-7	3 1E-7	331	327	103
13367 350	1.3E-6	1 3E-6	1 3E-6	321	220	103	13386 832	1 3E-6	6.0E-7	7 5E-7	12 112	1111	023
13367 483	7 1E-7	4 0E-7	6.0E-7	541	532	023	13386 956	2.4E-6	2.5E-6	2.4E-6	505	414	103
13367 725	1.6E-6	1.7E-6	1.6E-6	313	212	103	13387.628	2.0E-6	8.0E-7	4.9E-7	615	524	103
13367.957	2.2E-6	2.6E-6	2.7E-6	633	532	023	13387.628	2.0E-6	5.9E-7	5.3E-7	625	616	103
13368.199	7.0E-7	3.9E-7	6.0E-7	542	533	023	13387.628	2.0E-6	6.6E-7	6.1E-7	652	551	103
13369.002	6.4E-7	3.1E-7	1.9E-7	752	743	023	13387.628	2.0E-6	6.6E-7	6.1E-7	651	550	103
13369.265	5.4E-7	3.1E-7	1.9E-7	753	744	023	13388.013	2.4E-6	2.4E-6	2.6E-6	414	303	103
13369.856	1.7E-6	1.9E-6	1.9E-6	212	101	103	13389.033	5.9E-7	2.1E-7	2.8E-7	321	202	023
13369.990	5.7E-7	4.7E-8	1.5E-7	836	817	023	13389.033	5.9E-7	3.8E-7	1.5E-7	735	726	103
13370.168	1.6E-6	1.5E-6	1.6E-6	432	331	103	13389.185	1.8E-6	1.8E-6	1.6E-6	515	414	103
13370.168	1.6E-6	3.6E-7	4.5E-7	440	431	023	13390.210	9.9E-7	2.9E-7	3.7E-7	13 013	12 012	023
13370.328	5.3E-7	3.5E-7	4.5E-7	441	432	023	13390.210	9.9E-7	1.8E-8	1.8E-8	13 113	12 012	023
13370.486	1.7E-6	1.5E-6	1.6E-6	431	330	103	13391.140	2.1E-6	2.2E-6	2.0E-6	524	423	103
13370.486	1.7E-6	7.3E-7	4.0E-7	514	423	103	13391.437	2.2E-6	2.1E-6	1.8E-6	413	312	103
13371.113	6.3E-7	8.4E-7	7.7E-7	221	212	103	13391.669	7.7E-7	1.3E-6	6.7E-7	836	735	023
13371.929	3.4E-6	3.4E-6	4.3E-6	919	818	023	13391.783	1.9E-6	1.6E-6	1.7E-6	643	542	103
13372.170	4.4E-7	7.3E-7	3.4E-7	633	624	103	13391.783	1.9E-6	2.2E-7	7.8E-8	836	827	103
13372.170	4.4E-7	7.1E-8	8.8E-8	735	716	023	13391.942	1.9E-6	1.6E-6	1.7E-6	642	541	103
13372.422	3.5E-6	3.4E-6	4.3E-6	909	808	023	13392.163	3.5E-7					
13372.623	2.9E-7	2.9E-7	1.12-/	615	616	103	13392.423	3.2E-7	3.7E-7	1.5E-7	625	514	023
13372.623	2.9E-7	1.0E-7	3.2E-8	919	808	023	13392.813	4.1E-/	175 (	1 (	= 0 =	4.0.4	102
13372.956	3.3E-/	3.3E-/	2.2E-/	052	043	1023	13393.189	1.8E-0	1./E-0	1.0E-0	505	404	103
133/3.231	1.4E-0	1./E-0	1.0E-0	202	202	103	13393.472	J.ZE-7	3./E-/	3.3E-/	/20	/1/	103
13373.946	6.4E.6	1.1E-0 6.0E-6	1.0E-0 8.6E-6	522	513	023	13393.973	4.40-7	2.35-7	2.3E=/ 2.7E_6	817	000 716	022
13374.165	2.0E-6	2.3E-6	2.2E-6	404	313	1023	13304 518	4.1E-6	1.6E-6	2.1E-6	017	827	023
13375 302	4.0E-6	4.2E-6	5.1E-6	726	625	023	13395 325	3.5E-6	3.5E-6	4.0E-6	725	624	023
13376 107	4.0E-0	2.5E-7	1.8E-7	551	542	023	13395 420	2.5E-6	2.5E-6	2.5E-6	515	404	103
13376 107	4 3E-7	2.5E-7	1.8E-7	550	541	023	13396 755	1.8E-6	1.6E-6	1.7E-6	221	110	103
13376.799	2.1E-6	1.2E-6	1.3E-6	542	441	103	13397.276	2.3E-6	2.3E-6	2.2E-6	606	515	103
13376.799	2.1E-6	1.2E-6	1.3E-6	541	440	103	13397.684	4.6E-7	3.1E-7	8.9E-8	726	615	023
13376.963	1.6E-6	1.8E-6	1.5E-6	312	211	103	13398.331	2.2E-6	2.2E-6	2.2E-6	634	533	103
13377.192	5.1E-7	8.6E-7	4.2E-7	532	523	103	13398.436	1.5E-6	1.6E-6	1.3E-6	616	515	103
13377.706	3.2E-6	1.0E-6	9.6E-7	423	414	103	13398.764	1.1E-6	9.6E-7	1.1E-6	331	220	023
13377.706	3.2E-6	2.1E-6	2.6E-6	10 110	919	023	13399.153	1.1E-6	9.5E-7	1.1E-6	330	221	023
13377.975	2.3E-6	2.1E-6	2.6E-6	10 010	909	023	13399.410	4.5E-7	2.8E-7	2.0E-7	762	661	103
13378.634	5.4E-6	5.1E-6	5.9E-6	624	523	023	13399.410	4.5E-7	2.8E-7	2.0E-7	761	660	103
13378.948	1.8E-6	1.9E-6	1.7E-6	414	313	103	13399.782	2.3E-6	2.3E-6	2.1E-6	523	422	103
13379.683	2.2E-6	2.2E-6	2.3E-6	313	202	103	13399.782	2.3E-6	1.6E-7	6.2E-9	1019	928	023
13380.302	3.4E-7	4.8E-7	2.7E-7	844	743	023	13399.912	1.6E-6	1.4E-6	1.5E-6	220	111	103
13381.692	7.3E-7	8.6E-7	4.3E-7	431	422	103	13400.414	4.5E-7					
13382.311	8.1E-7	8.3E-7	7.6E-7	524	515	103	13401.198	1.7E-6	1.5E-6	1.3E-6	606	505	103
13382.635	7.7E-7	4.3E-8	9.0E-7	11 011	10 110	023	13401.198	1.7E-6	6.2E-7	8.0E-7	937	836	023
13382.685	9.6E-7	1.2E-6	6.0E-7	11 111	10 110	023	13401.322	2.2E-6	2.2E-6	2.2E-6	633	532	103
13382.821	1.1E-6	1.2E-6	5.9E-7	11 011	10 010	023	13401.535	2.3E-6	1.1E-6	1.1E-6	835	734	023

is difficult, as the vibrational assignment provided by Ref. (8) is often ambiguous and levels with high  $K_a$  values appear to be perturbed through resonance interactions involving highly excited bending states.

In the case of the levels with low  $K_a$  values, the energy levels predicted by the effective Hamiltonian help to vibrationally assign the corresponding states among a number of predicted levels. However, the accuracy of such predictions degrades rapidly as J and  $K_a$  increase and becomes insufficient for an unambiguous vibrational assignment of the predicted (8) energy levels. In these circumstances, we could not identify which vibrational states are interacting with the energy levels of the (103) and (023) states for  $K_a \ge 5$  and  $J \ge 6$ . Most of these energy levels were therefore excluded from the fit.

Only two vibrational states, (151) and (260), were identified, on the basis of Ref. (8), as possible perturbers of the energy levels of the two states under study. The (260) state appears to be strongly linked to the (023) state through Coriolis-type interaction, while the (151) state is moderately mixed with the (023) state through Fermi resonance and with (103) state by Coriolis interaction. Moderate Fermi-

Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Vib.
Wavenumber		(cm <sup>-2</sup> /atm)	) .	$J K_{a} K_{c}$	J K <sub>a</sub> K <sub>c</sub>	State	Wavenumber		(cm <sup>-2</sup> /atm)		J Ka Kc	J Ka Kc	State
(cm <sup>-1</sup> )	Obs.	Calca	PS99°				(cm <sup>-1</sup> )	Obs.	Calca	PS99	l. <u></u> l		
13401.535	2.3E-6	1.8E-6	2.2E-6	918	817	023	13426.414	7.3E-7	5.3E-7	5.6E-7	10 010	919	103
13402.151	1.2E-6	2.5E-7	1.6E-8	918	919	103	13426.414	7.3E-7	5.5E-7	2.4E-7	10 110	919	103
13402.151	1.2E-6	5.6E-7	1.2E-6	1029	928	023	13430.531	1.0E-6	1.6E-7	4.5E-9	551	542	103
13402.348	2.2E-6	2.3E-6	2.2E-6	616	505	103	13430.531	1.0E-6	8.8E-7	7.1E-7	928	827	103
13402.612	1.9E-6	2.0E-6	1.9E-6	625	524	103	13430.816	1.8E-6	1.9E-6	1.8E-6	125	624	103
13402.923	1.9E-6	7.3E-7	4.4E-7	716	625	103	13431.008	1.0E-6	9.1E-7	9.9E-7	625	514	103
13402.923	1.9E-6	7.8E-7	7.1E-7	753	652	103	13431.488	5.7E-7	2.1E-7	3.5E-7	11 011	10 110	103
13402.923	1.9E-6	7.7E-7	/.IE-/	152	651	103	13431.488	5./E-/	4.4E-/	9.9E-8	11 111	10 110	103
13403.182	3.3E-7	a a E (	1.00.4			102	13432.058	5.9E-7	5 4F 7	e en e	10.00	0.0.7	022
13404.575	2.0E-6	2.2E-6	1.8E-6	514	413	103	13432.225	/.8E-/	5.4E-/	5.5E-/	1028	927	023
13405.7146	4.3E-7	1.1E-/	9.3E-8	928	919	103	13432.572	1.4E-6	1.2E-6	1.0E-6	817	/16	103
13406.142	1.9E-6	1.9E-6	1.8E-6	707	616	103	13432.710	2.0E-6	1.6E-6	1.3E-0	331	220	103
13406.722	1.2E-6	1.2E-6	9.9E-/	/1/	616	103	13432.771	2.2E-0	8.6E-/	1.3E-6	441	330	023
13406.816	1.0E-0	1.4E-0	1.0E-0	744	043	103	13432.771	2.2E-0	0./E-/	1.3E-0	440	221	023
13407.142	1.0E-6	9.2E-7	1.2E-0	1019	918	1023	13433.093	1.56-0	1.0E-0	1.35-0	330	221	103
13407.352	1.7E-0	1.4E-0	1.0E-0	143	042	103	13433.767	/.IE-/	4.4E-7	4.0E-7	955	854	103
13407.352	1./E-0	1.1E-/	3.3E-9	2.2.2	1029	1025	13434.103	3.3E-7	4.4E-/	2.8E-/	954	833	103
13408.154	1.4E-0	1.5E-0	1.0E-0	322	211	103	13434.493	5.5E-7	2.05.7	2.05.7	(14	5 3 3	021
13408.439	9.3E-7	1.2E-0	9.8E-7	107	000	103	13434.781	3.3E-1	3.8E-/	2.0E-7	034	523	023
13408.394	1.7E-7	4.4E-/	3.9E-7	422	2029	023	13434.890	4.4£-/	7 35 7	7 25 7	046	015	102
12400.009	4.26-7	3.JE-/	1 0E 4	422	505	1025	12426 002	0.7E-7	1.2E-7	1.2E-7	940	045	103
13409.020	1.76-0	1.96-0	1.00-0	016	725	022	13430.992	9.7E-7	9.7E-7	9.2E-7	937	030	103
13410.230	2.2E-0	2.2E-0	4.4 <b>C-</b> 0	020	123	023	13437.090	0./E-/ 0.4E-7	3.0E-7	4.ZE-/	1029	920	105
13411.404	J.0E-/	2157	105.8	10 2 0	10.010	102	13436.173	0.4E-/	8 25 7	5657	018	817	102
12411.057	1.10-0	2.1E-7 4.6E 7	1.9L-0	1029	1010	023	13438.373	7057	5 45 7	5 46 7	827	716	103
12411.037	1.75.6	1.0E-6	1.95.6	735	634	103	13430.041	9.7E.7	578.7	716.7	422	212	103
13411.940	6.7E-7	7.1E-7	7.0E-7	132	321	023	13440.085	7.8E-7	7 18-7	73E-7	922	844	103
13413.021	1.6E-6	1.7E-6	1.5E-6	726	625	103	13440.217	7.0E-7	3.8E.7	3.6E-7	945	817	103
13413 839	1.4E-6	1.7E-0	1.3E-6	808	717	103	13443 216	5.0E-7	5.3E-7	3.0E-7	1010	019	103
13414 123	8 1E-7	8 7E-7	6.7E-7	818	717	103	13443 808	1.5E-6	1.5E-6	1 3E-6	826	725	103
13414 500b	9.8E-7	6.8E-7	6.9E-7	431	322	023	13444 714	24E-7	1.56-0	1.52-0	020	125	105
13414.836	6.4E-7	3 1E-7	2.2E-7	863	762	103	13445 053	4.6E-7	2 5E-7	2 5E-7	10.2.9	918	103
13414 836	6.4E-7	3.1E-7	2.2E 7	862	761	103	13446 145	1.4E-6	1.2E-6	1.1E-6	432	321	103
13415 124	8 9E-7	8 6E-7	6.6E-7	808	707	103	13446 407	1.1E-6	4 8E-7	8 7E-7	541	432	023
13415 402	1.4E-6	1.5E-6	1 3E-6	818	707	103	13447 188	4 6E-7	1.1E-7	3 0E-9	431	414	103
13415.788	2.1E-6	2.2E-6	2.0E-6	624	523	103	13447.188	4.6E-7	3.2E-7	2.5E-7	11 110	1019	103
13415.989	1.8E-6	1.9E-6	1.6E-6	615	514	103	13448.144	1.2E-6	1.2E-6	1.1E-6	431	322	103
13417.627	1.5E-6	1.3E-6	1.5E-6	423	312	103	13448.455	2.9E-7	2.2E-7	5.9E-8	836	725	023
13418.076	1.8E-6	1.8E-6	1.9E-6	734	633	103	13448.721	3.1E-7	2.8E-7	2.1E-7	633	524	023
13418.166	5.7E-7						13449.176	2.3E-7	2.5E-7	6.8E-8	422	303	103
13418.338	1.1E-6	6.4E-7	5.4E-7	853	752	103	13449.375	3.5E-7	2.7E-7	2.3E-7	1056	955	103
13418.338	1.1E-6	3.2E-7	5.9E-7	936	835	023	13449.491	6.3E-7	4.7E-7		854	963	004
13418.488	1.2E-6	9.8E-7	1.1E-6	321	212	103	13449.609	5.7E-7	4.7E-7		853	964	004
13418.650	2.8E-7						13449.766	3.5E-7	9.7E-8	2.4E-7	937	826	023
13418.956	4.4E-7						13451.413	5.4E-7	4.2E-7	4.4E-7	1047	946	103
13419.126	3.5E-7						13453.656	2.2E-7					
13419.339	3.6E-7	2.0E-7	1.7E-7	1139	1038	023	13454.030	1.7E-6	8.3E-7	8.5E-7	551	440	023
13420.563b	1.2E-6	1.1E-6	9.1E-7	909	818	103	13454.030	1.7E-6	8.3E-7	8.5E-7	550	441	023
13420.689	6.4E-7	5.5E-7	4.0E-7	919	818	103	13458.056	8.2E-7	8.9E-7	8.6E-7	533	422	103
13421.245	4.8E-7	5.5E-7	3.9E-7	909	808	103	13458.180	4.4E-7	4.2E-7	4.1E-7	1046	945	103
13421.377	9.9E-7	1.1E-6	9.1E-7	919	808	103	13458.489	2.8E-7	1.9E-7	3.0E-7	1139	1038	103
13421.892	1.3E-6	1.1E-6	1.1E-6	845	744	103	13458.863	5.3E-7	2.9E-7	5.4E-7	643	532	023
13422.329	1.3E-6	1.3E-6	1.1E-6	827	726	103	13459.777	4.3E-7	2.6E-7	5.3E-7	642	533	023
13422.766	1.3E-6	1.2E-6	1.2E-6	927	826	023	13460.215	1.9E-7					
13423.337	1.4E-6	1.1E-6	1.1E-6	844	743	103	13460.367	1.1E-7					
13424.774	1.6E-6	1.4E-6	1.4E-6	836	735	103	13460.691	2.5E-7	3.0E-7	2.3E-7	624	505	023
13425.191	1.2E-6	1.1E-6	1.2E-6	524	413	103	13465.229	3.1E-7	2.8E-7	3.8E-7	523	414	103
13425.296	1.3E-6	1.5E-6	1.3E-6	716	615	103	13465.529	3.0E-7					

**TABLE 1**—Continued

type resonance was also found to take place between the (103) and (023) states.

The parameters obtained from the fitting to 150 experimental energy levels of the total number of 197 levels are presented in Table 3 with 65% confidence intervals. Parameters without confidence intervals were fixed to their initial estimated values. The rms deviation provided by variation of 28 parameters is  $0.05 \text{ cm}^{-1}$ , i.e., significantly larger than the averaged experimental uncertainty ( $0.007 \text{ cm}^{-1}$ ) of the levels derived from the combination difference of two and more lines. The observed distortion in the signs and values of the spectroscopic parameters.

eters especially for the (103) state probably arises from the influence of the dark states which could not be assigned and included in the fitting process. It is then not surprising to observe strong deviations between the levels calculated from the parameters listed in Table 3 and the experimental values for the levels excluded from the fit. The corresponding transitions (40 in all) were, in fact, assigned using line center predictions of Ref. (8).

During the course of this analysis, a new dipole-moment surface (DMS) for  $H_2O$  became available (13). Thus new calculations of the HDO spectrum were carried out to make the

**TABLE 1**—Continued

Observed		Intensity		Upper	Lower	Vib.	Observed		Intensity		Upper	Lower	Víb.
Wavenumber		(cm <sup>-2</sup> /atm)	)	J Ka Ke	J Ka Kc	State	Wayenumber		(cm <sup>-2</sup> /atm)	)	J Ka Kc	J Ka Kc	State
(cm <sup>-1</sup> )	Obs.	Calc. <sup>a</sup>	PS99 <sup>b</sup> )				(cm <sup>-1</sup> )	Obs.	Calc <sup>-a</sup>	PS99 <sup>b</sup>			
13465.658	7.1E-7	4.5E-7	3.6E-7	661	550	023	13475.896	3.4E-7	3.8E-7	4.1E-7	735	624	103
13465.658	7.1E-7	4.5E-7	3.6E-7	660	551	023	13477.504	7.6E-7	2.7E-7	2.2E-7	762	651	023
13466.111	1.2E-6	1.7E-6		753	862	004	13477.504	7.6E-7	2.7E-7	2.2E-7	761	652	023
13466.111	1.2E-6	1.7E-6		752	863	004	13482.740	3.1E-6	3.0E-6		651	762	004
13466.605	1.1E-6	5.5E-7	5.4E-7	652	541	023	13482.740	3.1E-6	3.0E-6		652	761	004
13466.605	1.1E-6	5.5E-7	5.4E-7	651	542	023	13483.668	8.5E-7	9.0E-7	3.6E-7	541	432	103
13467.448	4.6E-7	5.8E-7	5.1E-7	1028	927	103	13484.171	5.5E-7					
13467.991	5.4E-7	6.0E-7	6.1E-7	634	523	103	13487.285	3.6E-7	2.3E-7	2.5E-9	642	625	103
13468.900	7.2E-7	1.3E-6	4.1E-7	441	330	103	13488.044	5.0E-7	3.4E-7	3.0E-7	1138	1037	103
13468.900	7.2E-7	1.3E-6	4.1E-7	440	331	103	13488.840	4.5E-7	1.6E-7	1.3E-7	863	752	023
13469.600	4.2E-7	2.2E-7	1.2E-7	771	660	023	13488.840	4.5E-7	1.6E-7	1.3E-7	862	753	023
13469.600	4.2E-7	2.2E-7	1.2E-7	770	661	023	13491.653	2.8E-7	2.6E-7	1.4E-7	734	615	023
13471.906	4.5E-7	6.1E-7	5.7E-7	1037	936	103	13491.737	2.7E-7					
13474.206	5.7E-7						13499.336	4.7E-6	4.6E-6		551	660	004
13475.355	4.6E-7						13499.336	4.7E-6	4.6E-6		550	661	004

best possible predictions. In these calculations, we used the same potential energy surface as used previously (8). The new calculations differ from our previous work (8) in two aspects.



**FIG. 1.** Comparison of the overview of the stick spectrum of the  $v_1 + 3v_3$  and  $2v_2 + 3v_3$  bands of HDO in the 13 165–13 500 cm<sup>-1</sup> spectral region: (a) Extracted from the ICLAS spectrum. The absolute intensities were normalized to the total absorption intensity predicted in this spectral region in Ref. (*13*). (b) Simulated by the effective Hamiltonian with the parameter values listed in Table 3 with the same normalization of the intensities as in (a). (c) Predicted from the *ab initio* calculations of Ref. (*13*). (d) Predicted from the *ab initio* calculations of Ref. (*8*). Note that the intensity scale is twice as much as in (b) and (c).

First, we used the new more accurate DMS (13), and second, we took advantage of increased computing facilities to carry out calculations using larger rovibrational basis sets. In these calculations we computed all eigenvalues with energies up to  $0.11 E_h$  above the minimum, and we based our basis functions on a self-consistent field (SCF) calculation on the lowest rotation-bending level with  $v_1 = v_3 = 1$ . In the final diagonalization, we included all functions with sums of SCF energies up to 0.19  $E_h$  above the minimum, except the maximum energy stretching function had energy  $\leq 0.15 E_h$ , and the maximum energy rotation-bending function had energy  $\leq 0.17 E_h$ . The maximum number of functions in the final diagonalization was limited to 3000, and calculations were carried out for J up to 30.

The comparison of these new calculations with the experimental energy levels is presented in Table 2. The improvement of these new results compared to Ref. (8) is clear, especially for levels with high J values. The largest deviation between observed and calculated line centers decreases from -2.6 to -0.3cm<sup>-1</sup>, while the new rms deviation is 0.13 cm<sup>-1</sup> compared to  $0.71 \text{ cm}^{-1}$  for the predictions of Ref. (8). Finally using the new calculations of Ref. (13), we could identify about 20 additional transitions involving highly excited levels of the (103) vibrational state such as the [872]-[871], [871]-[872] doublet of the  $\nu_1 + 3\nu_3$  band at 13 286.297 cm<sup>-1</sup>. The observed line positions are presented in Table 1 with, when available, their rotational and vibrational assignments. Overall 350 absorption transitions were attributed to the  $v_1 + 3v_3$  band, while 316 of them belong to the  $2\nu_2 + 3\nu_3$  band. It should be noted that our vibrational assignments are frequently inverted compared to those of Ref. (13) especially for the lines involving high  $K_a$ . Six lines were found to belong to the  $4\nu_3$  band (1). Only 7% of the observed HDO lines were left unassigned. Part of them may belong to the D<sub>2</sub>O isotope species. Some lines, marked by "b" in Table 1, are probably blended by  $H_2^{16}O$  lines in accordance with the line lists given in Refs. (7) and (14). It is interesting to note (see also Ref. (15)) that rather strong HDO lines in the 13 390-13 400 cm<sup>-1</sup> region were erroneously presented as unidentified  $H_2^{16}O$  lines in the line list attached to Ref. (14).



FIG. 2. Comparison of the HDO absorption spectrum in the 13 269.3-13 283.8 cm<sup>-1</sup> spectral region. (a) ICLAS spectrum recorded with an equivalent path length of 15 km and a total vapor pressure of 14 Torr. (b) Synthetic spectrum obtained from the effective Hamiltonian approach. Note that in spite of the excellent agreement, a spurious cluster of lines (marked by  $\times$ ) is predicted. These lines, not observed experimentally, are induced by an intensity transfer to the (260) dark state introduced in the EH model. The  $J'K'_aK'_c$ - $J''K''_{a}K''_{c}$  rotational assignments are given for all the lines with an intensity larger than  $1.3 \times 10^{-6}$  cm<sup>-2</sup>/atm. The rotational assignments written in bold characters are related to the (103) vibrational state, while the others correspond to the (023) vibrational state. (c) Calculated spectrum provided by the new ab initio predictions from Ref. (13) in excellent agreement with the experimental spectrum. (An almost constant deviation of 0.1 cm<sup>-1</sup> to the higher frequency is observed in this range.) The A and B type of the transitions is indicated for the  $v_1 + 3v_3$  to stress the change and improvement in the prediction of the intensities compared to (d). (d) Calculated spectrum provided by the ab initio predictions from Ref. (8). Note that the intensity scale is twice as much as in (b) and (c). The A and B type of the transitions of the  $\nu_1 + 3\nu_3$  band is given.

The parameters of the transformed dipole moment of the (103) and (023) states were obtained using the approach presented in Ref. (16) from the fitting to 421 experimental intensities of 590 values initially introduced into the fitting process. The rms deviation achieved by variation of 25 parameters for both A- and B-type transitions is of 9.8%, i.e., close to the experimental accuracy of the well-resolved isolated lines. Still

the calculated intensities of some transitions involving perturbed high  $K_a$  energy levels are significantly (up to three times) overestimated (see Table 1) showing that the resonance scheme adopted is probably incomplete. Figures 1–3 show a comparison between the experimental and EH synthetic spectrum for the whole spectrum and two expanded regions. The overall agreement is satisfactory and the EH predictions can then reliably be used at least for an unambiguous rovibrational assignment of most of the absorption lines.

It is interesting to note that, except for a few levels of the (260) state interacting with levels of the (023) state, the resonance interactions with the two dark states introduced in the EH, in fact, do not induce sufficient intensity transfer from the  $\nu_1 + 3\nu_3$  and  $2\nu_2 + 3\nu_3$  lines to allow the experimental observation of extra lines. Moreover, the strongly perturbed



**FIG. 3.** Same as Fig. 2 for the 13 366–13 376 cm<sup>-1</sup> spectral region. Note the drastic improvements between the predictions of (8) and (13). For instance, the change in the relative intensities of the four lines close to 13 370 cm<sup>-1</sup> shows that the hybrid character of the  $\nu_1 + 3\nu_3$  band is much better reproduced by the new predictions. Note also that the line positions of the  $2\nu_2 + 3\nu_3$  band were predicted in Ref. (8) with a shift up to 1 cm<sup>-1</sup> from the experimental values. On the other hand, extremely weak features predicted by the new calculations (13) are detectable at the experimental noise level and not reproduced by the EH simulation.

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 TABLE 2

 Rotational Energy Levels (cm<sup>-1</sup>) of the (103) and (023) Vibrational States of HDO

			(0 )	2 3)						(103)		
$J K_a K_c$	Eobs	$\sigma$	N	obs-cal	$\Delta_l$	$\Delta_2$	Eobs	σ	Ν	obs-cal	$\Delta_l$	$\Delta_2$
000	13278.358	5.3	2	-0.001	-0.08	-0.08	13331.612	2.0	2	0.001	-0.13	-0.13
101	13293.683	4.5	4	-0.010	-0.09	-0.09	13346.634	6.1	4	0.002	-0.13	-0.13
111	13307.877	8.4	3	-0.004	-0.08	-0.08	13358.263	5.1	5	0.037	-0.13	-0.13
110	13311.159	1.8	3	-0.027	-0.09	-0.09	13361.143	8.2	3	0.038	-0.13	-0.13
202	13323.820	6.5	4	-0.014	-0.08	-0.08	13376.198	4.1	4	0.004	-0.17	-0.16
212	13335.207	7.7	6	0.007	-0.09	-0.09	13385.368	3.2	6	-0.032	-0.12	-0.12
211	13345.080	1.9	4	-0.016	-0.08	-0.08	13394.090	4.9	4	0.053	-0.13	-0.13
221	13386.910	7.8	4	-0.082	-0.08	-0.08	13429.248	7.5	5	0.049	-0.11	-0.11
220	13387.488	7.6	3	-0.008	-0.09	-0.08	13429.716	3.6	4	0.041	-0.12	-0.11
303	13367.776	4.7	5	-0.035	-0.12	-0.08	13419.425	1.8	5	-0.001	-0.15	-0.12
313	13375.910	6.7	6	0.035	-0.11	-0.08	13425.857	6.1	7	-0.015	-0.15	-0.13
312	13395.528	2.1	5	-0.033	-0.09	-0.09	13443.153	3.4	6	0.051	-0.13	-0.13
322	13432.710	4.0	2	-0.051	-0.09	-0.08	13474.338	4.3	6	0.054	-0.12	-0.12
321	13435.199	6.9	2	0.001	-0.12	-0.09	134/6.622	4.8	6	0.036	-0.15	-0.12
331	13508.027	7.3	5	-0.020	-0.10	-0.08	13541.979	1.9	4	-0.035	-0.13	-0.10
330	13308.069	1.2	3	-0.025	-0.09	-0.09	13342.023	5.5	4	-0.042	-0.11	-0.11
404	13424.497	0.0 7.5	5	-0.029	-0.20	-0.08	134/3.337	5.0	2	0.001	-0.20	-0.13
414	13429.036	67	6	-0.039	-0.19	-0.08	13479.339	11.0	6	-0.025	-0.21	-0.13
413	13402.001	1.4	4	-0.039	-0.12	-0.09	13534.092	3.6	5	0.059	0.14	-0.12
423	13500.210	7.5	1	-0.007	-0.10	-0.00	13540.478	10	7	0.003	-0.15	-0.12
432	13569 558	71	6	0.004	-0.17	-0.09	13603 199	78	5	-0.002	-0.19	-0.13
431	13569 889	53	6	0.004	-0.17	-0.09	13603 535	52	5	-0.017	-0.13	-0.10
441	13665 823	57	4	-0.054	-0.10	-0.09	13701 943	59	3	-0.021	-0.12	-0.09
440	13665.837	10.0	4	0.018	-0.14	-0.07	13701.946	6.9	2	-0.022	-0.21	-0.18
505	13493.174	5.7	4	-0.023	-0.27	-0.09	13543.339	4.1	3	0.015	-0.23	-0.13
515	13496,154	5.0	4	0.053	-0.26	-0.08	13545.568	6.3	3	-0.025	-0.24	-0.13
514	13543.662	7.4	4	-0.051	-0.18	-0.09	13587.552	7.3	5	0.028	-0.21	-0.14
524	13568.436	6.5	6	0.026	-0.16	-0.08	13608.177	4.9	6	0.034	-0.20	-0.12
523	13582.802	6.7	6	0.051	-0.32	-0.09	13621.612	3.0	6	-0.087	-0.33	-0.13
533	13646.527	6.2	6	0.013	-0.28	-0.09	13679.890	6.4	4	-0.004	-0.34	-0.11
532	13647.802	5.4	5	0.043	-0.17	-0.09	13681.186	0.1	2	-0.025	-0.19	-0.11
542	13741.888	3.3	2	0.027	-0.12	-0.07	13779.134	5.9	2	0.021	-0.18	-0.07
541	*13741.899	8.3	5		-0.23	-0.10	13779.163	8.1	2	0.015	-0.35	-0.08
551	*13856.355	5.4	2		-0.20	-0.08	*13910.758	11.5	2		-0.36	-0.09
550	*13856.362	3.5	2		-0.12	-0.08	*13910.758	10.9	2		-0.19	-0.09
606	13573.527	1.9	3	-0.011	-0.47	-0.08	13623.133	7.8	5	0.024	-0.37	-0.13
616	13575.127	4.1	4	0.049	-0.48	-0.08	13624.295	3.4	4	-0.022	-0.26	-0.13
615	13639.424	3.0	3	-0.046	-0.23	-0.08	13681.231	6.4	4	0.025	-0.24	-0.13
625	13657.637	5.5	5	0.133	-0.25	-0.11	13696.247	5.6	4	0.002	-0.24	-0.12
624	13682.634	3.4	4	0.052	-0.42	-0.09	*13719.780	3.3	5	0.000	-0.42	-0.13
634	13/38.///	4.1	3	-0.036	-0.36	-0.09	13//1.988	5.6	4	-0.003	-0.42	-0.10
633	13/42.366	0.8	4	0.045	-0.20	-0.10	13775.724	5.4	3	0.013	-0.25	-0.10
643	13833.209	5.2	4	0.039	-0.19	-0.10	138/2.024	1.0	2	0.020	-0.33	-0.08
642	*13833.440	0.3	2		-0.29	-0.10	138/2.190	8.1 6.1	3	0.019	-0.48	-0.08
651	*13046.840	1.4	2		-0.23	-0.10	*14003.600	0.1	2		-0.45	-0.08
661	*14081.677	1.4	1		-0.22	-0.08	*14005.802	4.4	2		-0.55	-0.08
660	*14081.627		i		-0.22	-0.08	*14164.061	82	2		-0.34	-0.08
707	13665 561	6.8	2	-0.003	-0.49	-0.09	13714 756	3.9	4	0.035	-0.44	-0.09
717	13666 374	11.5	5	0.043	-0.50	-0.10	13715 334	51	5	-0.021	-0.40	-0.15
716	13748.028	8.0	2	-0.018	-0.35	-0.08	13787.804	8.3	5	-0.012	-0.33	-0.14
726	13760.182	6.2	3	0.009	-0.35	-0.08	13797.910	8.3	4	0.003	-0.33	-0.12
725	13798.867	6.4	2	0.014	-0.63	-0.09	*13834.370	5.6	5	0.000	-0.69	-0.13
735	13846.080	0.7	3	-0.146	-0.58	-0.11	13879.461	3.6	4	0.131	-0.68	-0.07
734	13854.188	6.1	3	0.026	-0.33	-0.10	13887.742	7.3	3	-0.047	-0.43	-0.11
744	13940.059	0.6	2	0.028	-0.29	-0.11	13980.706	1.3	3	-0.022	-0.48	-0.09
743	*13940.671	0.9	2		-0.54	-0.13	13981.340	13.2	3	0.014	-0.85	-0.09
753	*14052.588		1		-0.46	-0.12	14112.079	8.8	3	0.008	-0.80	-0.09
752	*14052.612		1		-0.26	-0.11	14112.087	9.7	3	0.001	-0.46	-0.08
762	*14186.671		1		-0.23	-0.10	*14272.196	3.3	2		-0.43	-0.07

*Note.* Asterisks denote the energy levels excluded from the fitting.  $\sigma$  denotes the experimental uncertainties of the levels given in 10<sup>-3</sup> cm<sup>-1</sup>. *N* is the number of lines sharing the same upper level.  $\Delta_1$  is the difference between the experimental energy levels and the predictions of Ref. (8).  $\Delta_2$  is the difference between the experimental energy levels and the predictions of Ref. (13).

transitions correspond to high  $K_a$  values and are therefore themselves rather weak. This feature agrees with both the observation and the new predictions of Ref. (13). Only the transitions reaching the [202] and [633] rotational sublevels of the (0 11 0) and (1 5 1) states (rovibrational assignments of Ref. (13)) are predicted to have significant intensities (up to  $8.8 \times 10^{-7}$  cm<sup>-2</sup>/atm). However, we could identify only one line at 13 362.979 cm<sup>-1</sup> with an experimental intensity of  $6.4 \times 10^{-7}$  cm<sup>-2</sup>/atm corresponding to the [633]–[524] transition of the  $\nu_1 + 5\nu_2 + \nu_3$  band.

Similar to Refs. (1, 2), to give an estimation of the absolute intensities of the observed absorption lines, we normalized our relative experimental intensities on the total predicted (13)absolute intensity of the two bands. This normalization procedure is supported by the excellent agreement between predictions of Ref. (8) and recent accurate experimental measure-

			(0	2 3)						(103)		
$J K_a K_c$	$E_{obs}$	$\sigma$	N	obs-cal	$\Delta_l$	$\Delta_2$	$E_{obs}$	$\sigma$	N	obs-cal	$\Delta_l$	$\Delta_2$
761	*14186.670		1		-0.41	-0.10	*14272.196	3.3	2		-0.78	-0.09
771	*14342.390		1		-0.35	-0.08	14457.916		1	0.005	-0.69	-0.08
770	*14342.390		1		-0.19	-0.08	14457.916		1	0.005	-0.39	-0.07
808	13769.326		1	-0.138	-0.94	-0.12	13818.285	0.4	2	0.031	-0.66	-0.16
818	13769.737		1	0.021	-0.94	-0.11	13818.570	5.1	4	-0.016	-0.66	-0.16
817	13868.440	3.0	4	0.082	-0.42	-0.09	13906.490	0.6	2	-0.040	-0.42	-0.14
827	13875.938	9.7	3	-0.021	-0.43	-0.11	13912.762	7.3	4	-0.046	-0.43	-0.14
826	13930.386	6.6	2	-0.045	-0.71	-0.11	*13963.931		1		-0.74	-0.19
836	13968.569	7.3	4	0.084	-0.69	-0.13	14001.685	7.3	2	0.051	-0.80	-0.13
835	13983.496		1	-0.015	-0.38	-0.15	14017.815	0.3	2	-0.101	-0.46	-0.12
845	14062.180		1	-0.064	-0.31	-0.13	14105.219	2.9	2	-0.088	-0.50	-0.09
844	*14063.912		1		-0.53	-0.14	14106.947		1	-0.028	-0.88	-0.12
853							*14236.357	6.0	2		-0.68	-0.07
863	*14306.853		1		-0.40	-0.10	*14395.975	11.4	2		-0.77	-0.09
862	*14306.846		1		-0.46	-0.10	*14395.975	11.2	2		-0.95	-0.11
872							14581.133		1	-0.005	-0.86	-0.11
871							14581.133		1	-0.005	-0.71	-0.09
909	13884.937		1	0.021	-1.11	-0.14	13933.765	5.0	2	0.029	-0.77	-0.17
919	13885.136		1	0.009	-1.11	-0.13	13933.894	1.2	2	-0.052	-0.79	-0.18
918	*14000.097		1		-0.76	-0.10	14036.936		1	0.023	-0.69	0.06
928	14004.464		1	-0.062	-0.73	-0.07	14040.483	5.5	2	-0.054	-0.73	-0.15
927	14075.859	4.6	2	-0.071	-0.82	-0.14						
937	*14102.867	12.3	2		-0.71	-0.12	14138.600	11.4	2	0.066	-1.04	-0.16
936	*14130.144		1		-0.60	-0.13						
946							*14245.267		1		-0.81	-0.12
945							14249.610		1	0.002	-1.12	-0.16
955							*14376.299		1		-1.07	-0.18
954							*14376.724		1		-0.82	-0.14
10.0.10	14012.403		1	-0.008	-1.15	-0.18	14061.205		1	0.017	-0.83	-0.20
10 1 10	14012.496		1	-0.010	-1.14	-0.17	14061.205		1	-0.028	-0.87	-0.24
1019	*14142.877		1		-0.76	-0.12	14178.951		1	0.033	-0.77	-0.15
1029	*14145.248		1		-0.83	-0.12	14180.787	0.3	2	-0.049	-0.81	-0.16
1028	14233.868	0.8	2	0.070	-0.77	-0.18	*14269.091		1		-1.04	-0.18
1037							14331.304	5.5	2	-0.043	-1.00	-0.15
1047							*14400.990		1		-1.04	-0.13
1046							14409.815		1	0.078	-1.13	-0.18
1056							*14532.160		1		-2.14	-0.20
11011	14151.751	0.4	2	-0.005	-2.40	-0.27	14200.604		1	-0.011	-1.58	-0.23
ппп	14151.801	0.4	2	0.001	-2.41	-0.15	14200.604		1	0.038	-1.60	-0.25
11 1 10	*14296.922		1		-0.86	-0.16	14332.252		i	-0.006	-0.96	-0.20
11 2 10	*14298,169		1		-0.86	-0.16						
1139	*14415.132		1		-1.53	-0.20	14454.282		1	0.002	-2 42	-0.21
11.3.8							14512.612		1	0.024	-0.96	-0.16
12 1 12	14302.955		1	-0.007	-2.54	-0.18			-			
13 0 13	14465.924		1	-0.010	-2.58	-0.31						
13 1 13	14465.972		ī	0.029	-2.57	-0.30						
			. (1.5	(1)		0.00						
IKK	F.		$\frac{1}{N}$	obs-cal	4.	4.						
633	*13656.615	0	1	505 val	-2.23	-0.05						
	10000.010		1		-2.23	-0.05						

 TABLE 2—Continued

ments in the 4700–7700 cm<sup>-1</sup> spectral region (17-18) evidenced in Ref. (19). The very good coincidence of the experimental (a) and newly predicted (c) intensities (see Figs. 1–3) allowed us to make a reasonable normalization of the experimental and calculated (EH) intensities over the whole spectral region. After normalization, the comparison of the experimental line intensities with the predicted (13) values shows that 91% of them agrees within 22% of their predicted values.

In the lower part (d) of Figs. 1–3, the spectrum previously predicted in Ref. (8) is also given for comparison with the new prediction (13). Significant differences and improvements concerning the absolute intensities are noticed (see also Table 4). First, the total absorption intensity in the considered spectral region was reduced from  $3.29 \times 10^{-3}$  (Ref. 8) to  $1.30 \times 10^{-3}$  cm<sup>-2</sup>/atm (Ref. 13). Second, in the high energy part, the spectrum is much better reproduced by the new calculations. A detailed analysis of this region shows that the disagreement observed in the predictions of Ref. (8) concerns mainly the

intensity of the *A*-type transitions of the  $\nu_1 + 3\nu_3$  band. Indeed, Ref. (8) predicted *A*-type transitions approximately more than three times stronger than observed, while *B*-type transitions were calculated with intensities two times lower than the experimental values. This effect is particularly clear on the four lines observed just above 13 370 cm<sup>-1</sup> in Fig. 3.

The total *A*- and *B*-type intensities of the  $\nu_1 + 3\nu_3$  and the  $2\nu_2 + 3\nu_3$  bands calculated from our EH parameters, and from the predictions of Refs. (8) and (13), are collected in Table 4. The EH calculations were performed in the 13 000–13 560 cm<sup>-1</sup> spectral region, taking into account all the lines with intensity larger than  $1.0 \times 10^{-8}$  cm<sup>-2</sup>/atm. The new predictions (13) give nearly the same value for the *A*- and *B*-type transitions' total intensities of the  $\nu_1 + 3\nu_3$  band in agreement both with the experiment and the EH results. However, the previous calculations (8) predicted *A*-type integrated intensity about one order of magnitude larger than the *B*-type integrated intensity of this band. In other words, the strong hybrid character, starting from J = 0, of the  $\nu_1 + 3\nu_3$  band is well reproduced

	(0 2 3)	(1 0 3)	(1 5 1)	(2 6 0)
$E_v$	13278.359	13331.612	12986.67	13218.090
A	23.57591(650)	20.51032(430)	59.8704(530)	56.03481(860)
В	9.34158(190)	8.94251(140)	9.454	9.252
С	5.99274(110)	6.07555(110)	5.693	5.724
$\Delta_k$	5.584(100)×10 <sup>-2</sup>	-2.4818(230)×10 <sup>-2</sup>	2.50×10 <sup>-1</sup>	7.623
$\Delta_{ik}$	3.434(250)×10 <sup>-3</sup>	-8.943(480)×10 <sup>-4</sup>	-6.33×10 <sup>-3</sup>	-6.99×10 <sup>-2</sup>
$\Delta_i$	6.544(150)×10 <sup>-4</sup>	1.7949(650)×10 <sup>-4</sup>	7.25×10 <sup>-4</sup>	7.25×10 <sup>-4</sup>
$\delta_k$	9.668(290)×10 <sup>-3</sup>	-4.631(270)×10 <sup>-3</sup>	2.27×10 <sup>-2</sup>	2.27×10 <sup>-2</sup>
$\delta_i$	3.170(100)×10 <sup>-4</sup>	2.513(910)×10 <sup>-5</sup>	3.17×10 <sup>-4</sup>	3.17×10 <sup>-4</sup>
$\dot{H}_k$	7.00×10-4	4.6222(430)×10 <sup>-4</sup>	$1.46 \times 10^{-2}$	3.69
$H_{ki}$	-2.5668(920)×10 <sup>-4</sup>	. ,		

 TABLE 3

 Spectroscopic Constants of the (103), (023), (151), and (062) States of HDO (in cm<sup>-1</sup>)

	F <sub>k</sub>	$F_i$	F <sub>xy</sub>	$C_{v}$	$C_{xz}$
(023)-(103)	-2.617(230) ×10 <sup>-1</sup>	-9.047(250)×10 <sup>-2</sup>	-3.525(450)×10 <sup>-2</sup>		
(151)-(103)				1.2001(550)	5.2532(710) ×10 <sup>-1</sup>
(151)-(023)	-5.186(260) ×10 <sup>-1</sup>	1.579(310)×10 <sup>-2</sup>			
(062)-(023)					2.8050(400)×10 <sup>-1</sup>

**Coupling constants** 

by the new calculations (13), while the previous ones predicted a band with mostly A-type character. The  $2\nu_2 + 3\nu_3$  band has a strong B-type character well accounted for by the new calculations (13) but which was too pronounced in the previous calculations (8). Note that the difference in the total A- and B-type intensities obtained in the frame of the EH method and predicted in Ref. (13) is due to the fact that the two approaches give for some lines different vibrational assignment.

The predicted spectra in the 12 000–15 800 cm<sup>-1</sup> range provided in Refs. (8) and (13) are compared in Fig. 4. This comparison shows that the absolute intensity of all the bands except the  $\nu_1 + 3\nu_3$  and  $2\nu_2 + 3\nu_3$  bands under consideration are mostly unchanged. This indicates, in particular, that the normalization procedure of the absolute intensities that we used in our previous investigations of the  $4\nu_3$  (1) and  $\nu_2 + 4\nu_3$ (2) bands still hold with the new predictions (13). These results

TABLE 4Total Intensities of A- and B-Type Transitions for the $\nu_1 + 3\nu_3$  and the  $2\nu_2 + 3\nu_3$  Bands of HOD (in  $10^{-3}$  cm<sup>-2</sup>/ atm) in the 13 000–13 560 cm<sup>-1</sup> Spectral Region

		_	-	
State	type	Effective Hamiltonian	Ref.(8)	Ref.(13)
103	А	0.33	1.05	0.19
	В	0.25	0.12	0.20
023	А	0.71	1.94	0.81
	В	0.16	0.11	0.11
	Total	1.45	3.29	1.30

are consistent with our observations on  $H_2O(13)$ . There, we saw that the two dipole-moment surfaces gave very similar results for lower energy transitions but could differ significantly for high-energy transitions.

Finally, concerning line positions, Figs. 2 and 3 show that for these particular spectral regions, the stronger deviations between the predicted and observed spectrum concern the transitions of the  $2\nu_2 + 3\nu_3$  band with the highest *J* values. The quality of the new calculations (*13*) is highlighted in Fig. 3 by extremely weak features, at the limit of the experimental noise level which are fully predicted both in intensity and position.

# 4. CONCLUSIONS

The HDO absorption spectrum in the 13 165–13 500 cm<sup>-1</sup> region was experimentally recorded and theoretically treated for the first time, leading to the complete spectrum assignment and the derivation of 196 accurate energy levels of the (103) and (023) vibrational states. The new results (13) of the accurate variational calculations of the HDO line positions and intensities were intensively used in the process of the spectrum assignment as well as the calculations in the frame of the effective Hamiltonian method. One of the interesting features evidenced by the present analysis is the strong hybrid character of the  $\nu_1 + 3\nu_3$  band with nearly equal A- and B-type transition intensities. Due to this circumstance, this band, in spite of being at least two times weaker than the  $2\nu_2 + 3\nu_3$  band, has a larger number of observed transitions than the stronger band. This particular spectral region has given the opportunity to highlight the improvements of the *ab initio* predictions recently



**FIG. 4.** Comparison of the previous (13) and new (8) predictions for the HDO spectrum in the 12 000–15 800 cm<sup>-1</sup> range. The four observed bands were previously analyzed on the basis of their ICLAS spectra:  $5\nu_1$  in Ref. (20),  $\nu_1 + 3\nu_3$  and  $2\nu_2 + 3\nu_3$  in the present work,  $4\nu_3$  in Ref. (1),  $\nu_1 + 4\nu_3$  in Ref. (2). Note the change in the calculated absolute intensity of the  $\nu_1 + 3\nu_3$  and  $2\nu_2 + 3\nu_3$  bands.

performed by one of us on the basis of the same PES but with an improved dipole-moment surface. The improvements compared to Ref. (8) concern both the energy levels and the line intensities.

The analysis of the (103) and (023) vibrational states illustrates the limit of validity of the effective Hamiltonian approach in its conventional form when applied to the highly excited states of nonrigid molecules (see also the conclusions of Ref. (2)). Highorder resonance interactions involving simultaneous interaction with several "dark" vibrational states result in unstable fitting procedure. On the other hand, the variational approach developed in Refs. (8, 13) is based on a limited set of spectroscopic data but provides high-quality line positions and intensities predictions in a wide spectral range. However, the effective Hamiltonian method remains attractive since it is compact, well elaborated, and does not require large computer facilities.

# ACKNOWLEDGMENTS

O. Naumenko thanks the University Joseph Fourier of Grenoble for the Visiting Professorship, during which this work was carried out, and acknowledges as well the financial support from the Russian Foundation for Basic Researches, Grant 99-03-33210.

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