The near ultraviolet rotation-vibration spectrum of water

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A new *ab initio* linelist of water vibration-rotation transitions extending up to $26\,000$ cm^{-1} is presented. This linelist is used to analyze the near-ultraviolet portion of the long pathlength water absorption spectrum of Carleer *et al.* [J. Chem. Phys. **111**, 2444 (1999)]. A total of 299 of the 568 observed transitions between 21 400 and 25 232 cm^{-1} are assigned. These transitions belong to eight excited vibrational states: $(4,2)^-1$, $(7,0)^+0$, $(7,0)^-0$, $(6,0)^+2$, $(6,0)^-2$, $(7,0)^-1$, $(8,0)^-0$, and $(8,0)^-0$, in local mode notation. Only three of these states have been observed previously. Observed and calculated energy levels are presented for these vibrational states and the band origins are determined. © *2000 American Institute of Physics.* [S0021-9606(00)01020-5]

I. INTRODUCTION

Water vapor is responsible for 70% of the known absorption of sunlight in the Earth's atmosphere. However, it is now firmly established[1] that there is a serious problem with missing absorption in all models of the Earth's atmosphere. The search for the missing absorber has led to number of laboratory campaigns to measure the many weak water absorptions that occur in the near-infrared and throughout the visible region. These studies are bolstered by new theoretical techniques which use high accuracy variational methods as the basis for making spectral assignment[2–6] and modeling radiative transfer.[7,8]

The weakest water absorptions measured to date lie in the near ultraviolet region of the spectrum. This region was studied by Camy-Peyret *et al.*[9] who measured 199 absorption lines in the spectral range 21 400–25 230 cm^{-1}, of which they were able to assign 59 to transitions of H$_2$ ^{16}O. In a recent paper, henceforth refered to as I, Carleer *et al.*[10] reported the measurement of long pathlength water absorption spectra in the 13 098–25 320 cm^{-1} region. While the great majority of lines measured in I lie below 21 400 cm^{-1}, 599 lie above this wave number.

In I analysis of the new measurements was restricted to wave numbers below 21 400 cm^{-1} because the available linelists were found to be inadequate for wave numbers higher than this. Here we report the calculation of a new, *ab initio* linelist which covers the near-ultraviolet region. With the aid of this linelist we are able to make 241 new line assignments in this region. These assignments not only extend our knowledge of the three vibrational states analyzed by Camy-Peyret *et al.*,[9] but give information on five new vibrational states.

Two of the vibrational states form part of the 8ν polyad. This polyad is of interest because theoretical studies have suggested that its vibrational states should show considerable deviation from conventional spectral patterns.[11]

The paper is organized as follows. In the next two sections we summarize the experimental results and report the

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TABLE I. Summary of newly assigned transitions.

Band		Previous (Ref. 9)			This work			Band origin
Local	Normal	Normal	Lines	Levels	Lines		Levels	(cm^{-1})
mode	mode	mode			a	b		
$(4,2)^-1$	(115)				9	1	5	22 513.
$(7,0)^+0$	(700)	(502)	5	2	81	9	39	22 529.296
$(7,0)^-0$	(601)	(403)	42	20	54	3	15	22 529.445
$(6,0)^+2$	(620)				5	1	3	22 628.
$(6,0)^-2$	(521)				11	5	10	22 630.
$(7,0)^-1$	(611)				12	4	10	23 947.
$(8,0)^+0$	(800)				8	16	20	25 120.
$(8,0)^-0$	(701)	(503)	12	6	8	15	18	25 120.278

[a]Assignments confirmed by combination differences.
[b]Assignments made only by comparison with calculated linelists.

calculation of our new linelist. Section IV presents and discusses our spectral analysis; conclusions are given in Sec. V.

II. EXPERIMENTAL MEASUREMENTS

The measurements were performed using the Bruker IFS 120M high resolution Fourier transform spectrometer of the Laboratoire de Chimie Physique Moléculaire (Université Libre de Bruxelles) using 12 traversals of the 50 m base length White-type multiple reflection absorption cell of the Groupe de Spectrométrie Moléculaire et Atmosphérique (Université de Reims) giving an absorption path of 602.32 m. A 450 W xenon arc lamp was used as light source. Two detectors (a Si- and a GaF-diode) were used to record the spectral region up to 30 000 cm^{-1}, although no water absorption features were identified above 25 232 cm^{-1}. Spectra were recorded at 18 °C and a water pressure of 18.5 hPa.

In the blue-near-ultraviolet part (17 700–30 000 cm^{-1}) of the spectrum, the co-addition of 4096 interferograms (24 h of recording time) proved necessary to attain a S/N ratio of 2500. Line positions and other parameters were measured using program SPECTRA[12] which fits each feature to a Voigt profile. After removing features whose widths were too narrow to be genuine, 541 lines were measured in the 21 400 and 25 232 cm^{-1} region, with an estimate error in the line positions of 0.004 cm^{-1}. Further details of the experimental procedure can be found in Table I. A full list of these lines, including the linewidth, line intensity (in relative units), and approximate equivalent width can be obtained from the electronic archive (EPAPS).[13]

III. CALCULATIONS

To enable us to assign the near-ultraviolet spectrum it was necessary to compute a new set of water vibration-rotation energy levels and associated transitions. If, as here, one solves the nuclear motion Schrödinger equation using a variational procedure, the accuracy of the calculation is determined by the quality of the potential energy surface used. Additional errors are possible from the failure of the Born–Oppenheimer approximation, which is implicit in the use of such a potential.

There are two routes for constructing a potential: one is via *ab initio* electronic structure calculations, the other is by

refining the surface to reproduce known spectroscopic data. Partridge and Schwenke (PS)[2] computed a high accuracy *ab initio* potential energy surface for water and we employ their $V5Z+\Delta V^{core}$ Born–Oppenheimer surface. However, PS used this surface as the starting point for refining a spectroscopic potential. The linelist generated by PS[14] using their spectroscopic potential reproduces room temperature experiment to very high accuracy throughout the infrared and into the visible region. As is discussed below, however, their predictions become very erratic in the near-ultraviolet region of concern to us here.

Conversely, experience[6,15] has shown that purely *ab initio* procedures extrapolate much more reliably than calculations based on spectroscopically adjusted potentials. For this reason we chose to employ the best currently available *ab initio* approach in our calculations. PS's Born–Oppenheimer surface was augmented by the adiabatic correction of Zobov *et al.*[16] and the electronic relativistic correction of Császár *et al.*[17] Some allowance was made for nonadiabatic effects by using a hydrogen mass midway between the mass of a proton and a hydrogen atom.[16] Inclusion of the relativistic correction is particularly important for getting a good representation of states with high stretching excitation, which are the ones which concern us here.

Tests have shown[18] that this procedure reproduces the known vibrational band origins of H_2 ^{16}O with a standard deviation of 10.5 cm^{-1}. The major underlying problem with this potential is in the bending mode. The addition of a simple two parameter bend only function improves the vibrational standard deviation to 1.4 cm^{-1}.[18] It is this improved potential that we use here.

So far the linelist extends up to up to $J=14$, which is more than adequate for the near-ultraviolet region where even the low J transitions are weak. The calculations were performed within a discrete variable representation (DVR) using the DVR3D program suite[19] in Radau coordinates with x-axis embedded as the bisector of the HOH angle. As before,[20] we used 40 Gauss–Laguerre DVR points based on Morse oscillatorlike functions for the radial functions. However, following comments on the lack of angular convergence of previous studies,[21] 44 Gauss–(associated) Legendre DVR points were used in the angular coordinate. DVR3D uses a two-step procedure for considering rotational excitation: $300\times(J+1)$ functions from the first ''vibrational'' step were used to diagonalize the full, exact kinetic energy operator, rotation-vibration Hamiltonian.

Energies up to 26 000 cm^{-1} above the ground state were considered. Transition dipoles were computed using PS's dipole surface and program DIPOLE3. As we are concerned with room temperature spectra, only intensities for transitions starting from energy levels below 9000 cm^{-1} were actually computed.

IV. SPECTRAL ANALYSIS

As most of the transitions observed by Camy-Peyret *et al.*[9] remain unassigned, we considered their data alongside ours. There are 17 lines observed by Camy-Peyret *et al.* not seen in the present study, giving us a dataset of 558 lines in the 21 400 and 25 232 cm^{-1} region.

Our method of assigning lines was similar to, but not quite the same as, those used in previous studies.[4,5,10,15] First, the observed spectrum was scanned for particularly strong lines. These strong lines were then matched with candidate transitions in our computed linelist. Such tentative assignments were then confirmed if appropriate transitions predicted by combination differences were present in the spectrum. This procedure was repeated until transitions to several rotational levels of the same excited vibrational state had been assigned. As for every vibrational band, the error in the calculated energy is more or less uniform (see Table III) it is possible to identify a systematic band error. Using this band error additional, often weaker, transitions associated with the same excited vibrational state could be assigned. Where possible these were also confirmed using combination differences. So far we have assigned nearly all the strong transitions in the spectrum; only two remain unassigned, i.e., the lines at $22\,476.152$ and $22\,636.069$ cm^{-1}. Many weaker transitions have also been assigned.

Our analysis has assigned 241 new transitions in the near-ultraviolet region. A summary of these assignments are given in Table I and a full list is given in Table II. All the transitions start from the ground, (000), vibrational state. We find transitions to eight distinct excited vibrational states, a significant advance on the three observed by Camy-Peyret *et al.*[9]

How these excited states are designated is not completely straightforward, as witnessed by the model calculations of Rose and Kellman.[11] In I we found it more satisfactory to label stretching states above about 15 000 cm^{-1} using local modes rather than the more conventional normal modes. Furthermore this change led to relabeling many of the normal mode state designations. A similar situation exists here. We believe that vibrational states in the 20 000 plus cm^{-1} region are local modelike, with the possible exception of predominantly bending states[11] which we do not observe. The standard mapping between local and normal mode labels also strongly suggests that the normal mode vibrational labels used by Camy-Peyret *et al.*[9] are not the correct ones. We have, therefore, relabeled their excited vibrational states accordingly; see Table I. We should stress that this is just a relabeling exercise and our analysis fully supports the assignments of Camy-Peyret *et al.*, with only one exception.

The near-degeneracy between pairs of vibrational states that only differ by the parity of the local mode combination, as denoted by the superscripted sign, is a strong indicator that our local mode labeling is indeed correct. Furthermore, the states we observe are the local mode excitations one would expect to be the strongest.

Using the transitions assigned here and previously by Camy-Peyret *et al.*, it is possible to build up tables of energy levels for the excited states. Such tables are important for a number of applications, including making further spectral assignments and developing theoretical models. Tables III presents our energy levels along with those derived by Camy-Peyret *et al.* For the new assignments the tables give the number of assigned transitions to each of the energy levels. Assignments of transitions to levels reached by more than one transition can be regarded as secure. In some cases we

TABLE II. Assigned transitions in the near-ultraviolet. Intensities are given in arbitrary units.

ν/cm^{-1}	Int	J''	K_a''	K_c''	J'	K_a'	K_c'	Band	
21 410.5350	0.0012	4	1	3	3	1	2	$(5,0)^-3$	a
21 426.5086	0.0012	4	2	2	3	2	1	$(5,0)^-3$	a
22 249.5727	0.0012	5	5	1	6	5	2	$(7,0)^-0$	a
22 254.9605	0.0008	8	1	8	9	0	9	$(7,0)^+0$	a
22 275.6114	0.0008	3	3	0	4	4	1	$(7,0)^+0$	a
22 276.6871	0.0010	6	4	3	6	5	2	$(7,0)^+0$	a
22 279.7927	0.0019	5	4	2	6	4	3	$(7,0)^-0$	a,b
22 290.9806	0.0008	6	2	5	7	2	6	$(7,0)^-0$	a
22 294.5051	0.0034	6	1	5	7	2	6	$(7,0)^+0$	a,b
22 294.8905	0.0012	5	4	1	5	5	0	$(7,0)^+0$	a,b
22 296.0493	0.0029	6	2	5	7	1	6	$(7,0)^+0$	a,b
22 300.1327	0.0012	6	3	4	6	4	3	$(7,0)^+0$	a,b
22 312.9601	0.0024	5	2	3	6	2	4	$(7,0)^-0$	a,b
22 319.2594	0.0025	4	4	0	5	4	1	$(7,0)^-0$	a,b
22 319.4385	0.0010	4	4	1	5	4	2	$(7,0)^-0$	b
22 322.9149	0.0011	6	4	3	7	3	4	$(7,0)^+0$	a
22 323.6211	0.0018	5	1	4	6	2	5	$(7,0)^+0$	a,b
22 329.3680	0.0015	6	1	6	7	1	7	$(7,0)^-0$	a
22 330.2459	0.0006	6	0	6	7	1	7	$(7,0)^+0$	a
22 330.5237	0.0027	6	1	6	7	0	7	$(7,0)^+0$	a,b
22 332.2433	0.0057	5	2	4	6	2	5	$(7,0)^-0$	a,b
22 333.1594	0.0023	5	1	4	6	1	5	$(7,0)^-0$	a,b
22 342.5642	0.0008	5	2	4	6	1	6	$(7,0)^+0$	a,b
22 345.1026	0.0026	4	3	2	5	3	3	$(7,0)^-0$	a,b
22 345.3482	0.0012	5	3	3	5	4	2	$(7,0)^+0$	a
22 350.9795	0.0030	5	3	2	5	4	1	$(7,0)^+0$	a,b
22 352.0423	0.0014	2	2	1	3	3	0	$(7,0)^+0$	a
22 352.6943	0.0005	5	3	3	6	2	4	$(7,0)^+0$	a
22 352.8659	0.0010	4	1	3	5	2	4	$(7,0)^+0$	a
22 355.4929	0.0019	6	1	5	6	3	4	$(7,0)^-0$	a,b
22 357.5484	0.0038	4	2	2	5	2	3	$(7,0)^-0$	a,b
22 362.4272	0.0012	4	3	1	4	4	0	$(7,0)^+0$	a
22 364.9192	0.0089	5	0	5	6	1	6	$(7,0)^+0$	a,b
22 366.1994	0.0017	5	1	5	6	0	6	$(7,0)^+0$	a,b
22 381.5037	0.0014	5	2	4	5	3	3	$(7,0)^+0$	a
22 384.2932	0.0019	4	2	3	5	1	4	$(7,0)^+0$	a,b
22 390.3897	0.0010	6	2	4	6	3	3	$(7,0)^+0$	a
22 394.9823	0.0010	3	1	2	3	3	1	$(7,0)^-0$	a
22 395.4433	0.0021	4	0	4	5	1	5	$(7,0)^+0$	a,b
22 396.1039	0.0063	5	5	1	5	5	0	$(7,0)^-0$	a,b
22 396.7560	0.0145	4	1	4	5	0	5	$(7,0)^+0$	a,b
22 397.1103	0.0055	4	1	4	5	1	5	$(7,0)^-0$	a,b
22 397.7935	0.0006	6	2	5	6	2	4	$(7,0)^-0$	a
22 401.2457	0.0045	4	2	3	4	3	2	$(7,0)^+0$	a,b
22 402.4106	0.0011	4	3	2	5	2	3	$(7,0)^+0$	a
22 407.0498	0.0039	5	2	3	5	3	2	$(7,0)^+0$	a,b
22 408.4312	0.0009	5	3	2	6	2	5	$(7,0)^+0$	a
22 412.6790	0.0009	3	2	2	4	2	3	$(4,2)^-1$	a
22 423.3617	0.0053	4	0	4	4	2	3	$(7,0)^-0$	a,b
22 425.9154	0.0083	2	2	0	3	2	1	$(4,2)^-1$	a,b
22 426.1718	0.0044	5	4	2	5	4	1	$(7,0)^-0$	a,b
22 426.3863	0.0092	3	1	3	4	0	4	$(7,0)^+0$	a,b
22 428.1891	0.0025	2	1	1	3	1	2	$(4,2)^{-1}1$	b
22 429.8069	0.0018	3	0	3	4	0	4	$(7,0)^-0$	a
22 430.0134	0.0064	5	1	4	5	2	3	$(7,0)^+0$	a,b
22 430.7769	0.0031	2	2	1	3	2	2	$(4,2)^-1$	a,b
22 439.5119	0.0019	2	2	1	3	2	2	$(7,0)^-0$	a,b
22 441.4775	0.0131	4	4	0	4	4	1	$(7,0)^-0$	a,b
22 445.5632	0.0019	3	0	3	3	2	2	$(7,0)^-0$	a
22 446.5734	0.0018	4	0	4	4	1	3	$(7,0)^+0$	a
22 447.6685	0.0024	2	0	2	3	1	3	$(7,0)^+0$	a
22 453.2708	0.0031	4	1	3	4	2	2	$(7,0)^+0$	a
22 460.3440	0.0011	2	1	2	3	0	3	$(7,0)^+0$	a
22 465.2262	0.0033	4	3	2	4	3	1	$(7,0)^-0$	a
22 467.3556	0.0008	5	3	3	4	4	0	$(7,0)^+0$	a
22 467.7539	0.0110	3	1	2	3	2	1	$(7,0)^+0$	a,b

TABLE II. (*Continued*).

ν/cm^{-1}	Int	J''	K_a''	K_c''	J'	K_a'	K_c'	Band	
22 470.2540	0.0004	6	1	6	5	2	3	$(7,0)^+0$	[a]
22 470.6876	0.0009	1	0	1	2	1	2	$(7,0)^+0$	[a]
22 473.2122	0.0010	5	3	2	4	4	1	$(7,0)^+0$	[a]
22 474.9909	0.0090	3	0	3	3	1	2	$(7,0)^+0$	[a,b]
22 475.1601	0.0027	2	1	1	2	2	0	$(7,0)^+0$	[a,b]
22 478.5947	0.0016	3	1	3	3	1	2	$(7,0)^-0$	[a]
22 479.6443	0.0051	3	3	0	3	3	1	$(7,0)^-0$	[a,b]
22 489.2081	0.0007	5	5	1	6	3	4	$(7,0)^-0$	[a]
22 492.1588	0.0010	0	0	0	1	1	1	$(7,0)^+0$	
22 494.7394	0.0022	2	0	2	2	1	1	$(7,0)^+0$	[a]
22 495.6555	0.0013	6	1	5	5	3	2	$(7,0)^-0$	[a]
22 496.5758	0.0010	4	2	2	4	2	3	$(4,2)^-1$	[a]
22 497.2641	0.0026	2	1	2	3	2	1	$(6,0)^+2$	[a]
22 498.3380	0.0013	4	2	3	3	3	0	$(7,0)^+0$	[a]
22 499.1709	0.0015	6	2	4	6	2	5	$(7,0)^-0$	[a]
22 499.5281	0.0010	5	2	3	5	2	4	$(7,0)^-0$	[a]
22 500.7030	0.0030	3	1	2	4	2	3	$(6,0)^+2$	[a]
22 500.9131	0.0061	2	2	1	2	2	0	$(4,2)^-1$	[a]
22 501.3470	0.0010	2	2	0	3	0	3	$(4,2)^-1$	[a]
22 502.0842	0.0021	2	1	2	2	1	1	$(7,0)^-0$	[a]
22 503.1693	0.0172	2	2	0	2	2	1	$(4,2)^-1$	[a,b]
22 503.7061	0.0026	4	2	2	4	2	3	$(7,0)^-0$	[a]
22 503.9111	0.0035	6	3	4	6	2	5	$(7,0)^+0$	[a]
22 507.8119	0.0114	1	0	1	1	1	0	$(7,0)^+0$	[a,b]
22 509.6428	0.0043	2	2	1	2	2	0	$(7,0)^-0$	[a,b]
22 514.8273	0.0013	5	3	2	5	2	3	$(7,0)^+0$	[a]
22 516.4063	0.0012	5	2	3	5	1	4	$(7,0)^+0$	[a]
22 533.3423	0.0034	3	2	1	3	1	2	$(7,0)^+0$	[a]
22 537.9262	0.0027	3	1	2	3	1	3	$(7,0)^-0$	[a]
22 540.2440	0.0013	3	1	3	4	1	4	$(6,0)^-2$	
22 541.0852	0.0059	1	1	0	1	0	1	$(7,0)^+0$	[b]
22 541.2380	0.0016	2	1	1	2	0	2	$(7,0)^+0$	[a]
22 543.1420	0.0028	3	1	2	3	0	3	$(7,0)^+0$	[a]
22 543.3501	0.0007	2	2	0	2	1	1	$(7,0)^+0$	[a]
22 544.9047	0.0045	4	1	3	4	1	4	$(7,0)^-0$	[a,b]
22 545.0079	0.0052	3	1	2	2	2	1	$(7,0)^+0$	[a]
22 547.9679	0.0012	6	2	4	5	3	3	$(7,0)^+0$	[a]
22 548.3908	0.0009	5	4	2	4	4	1	$(7,0)^-0$	[a]
22 549.4416	0.0013	5	1	4	5	1	5	$(7,0)^-0$	[a]
22 551.9663	0.0008	3	2	2	4	2	3	$(6,0)^-2$	[a]
22 553.0155	0.0017	6	2	5	6	1	6	$(7,0)^+0$	[a,b]
22 555.1497	0.0009	2	1	1	3	1	2	$(6,0)^-2$	[a]
22 556.8315	0.0009	2	0	2	3	0	3	$(6,0)^-2$	
22 557.4110	0.0012	6	1	5	6	0	6	$(7,0)^+0$	[a]
22 559.5088	0.0025	3	2	2	3	1	3	$(7,0)^+0$	[a]
22 559.8039	0.0027	5	2	4	5	0	5	$(7,0)^-0$	[a]
22 562.7524	0.0037	4	1	3	3	2	2	$(7,0)^+0$	[a]
22 563.8255	0.0036	4	3	2	3	3	1	$(7,0)^-0$	[a]
22 572.6426	0.0010	2	1	2	3	0	3	$(6,0)^+2$	[a]
22 573.3331	0.0223	2	1	2	1	0	1	$(7,0)^+0$	[a,b]
22 574.5219	0.0021	2	1	2	2	2	1	$(6,0)^+2$	[a]
22 575.7319	0.0012	2	2	1	2	0	2	$(7,0)^-0$	[a,b]
22 576.1709	0.0153	5	1	4	4	2	3	$(7,0)^+0$	[a,b]
22 576.6045	0.0009	2	2	0	3	2	1	$(6,0)^-2$	[a]
22 578.3430	0.0038	3	1	3	2	0	2	$(7,0)^+0$	
22 579.7949	0.0123	4	0	4	3	1	3	$(7,0)^+0$	[a,b]
22 580.6797	0.0045	3	0	3	3	1	2	$(6,0)^+2$	
22 581.1562	0.0015	2	2	1	3	2	2	$(6,0)^-2$	[a]
22 581.4765	0.0007	4	1	4	3	1	3	$(7,0)^-0$	[a]
22 581.7696	0.0125	3	0	3	2	0	2	$(7,0)^-0$	[a,b]
22 584.3524	0.0034	6	2	5	5	2	4	$(7,0)^-0$	[a]
22 584.7462	0.0015	4	2	2	3	2	1	$(4,2)^-1$	[a]
22 584.8113	0.0013	5	2	4	4	2	3	$(7,0)^-0$	[a]
22 585.3419	0.0013	4	1	4	3	0	3	$(7,0)^-0$	[a]
22 586.3755	0.0066	4	1	3	3	1	2	$(7,0)^-0$	[a,b]
22 587.2939	0.0020	5	0	5	4	1	4	$(7,0)^+0$	[a]
22 587.4951	0.0058	7	1	6	6	2	5	$(7,0)^+0$	[b]
22 587.9456	0.0032	6	1	5	5	2	4	$(7,0)^+0$	[a]
22 588.9142	0.0041	8	1	8	7	0	7	$(7,0)^+0$	[a,b]
22 589.2473	0.0053	6	1	6	5	1	5	$(7,0)^-0$	[a,b]
22 590.1046	0.0063	6	0	6	5	1	5	$(7,0)^+0$	[a,b]
22 590.6050	0.0090	7	1	7	6	1	6	$(7,0)^-0$	[b]
22 590.7830	0.0033	5	1	5	4	0	4	$(7,0)^+0$	[a]
22 591.0989	0.0102	7	0	7	6	1	6	$(7,0)^+0$	[b]
22 591.4129	0.0051	6	1	6	5	0	5	$(7,0)^+0$	[a,b]
22 591.9649	0.0034	4	2	2	3	2	1	$(7,0)^-0$	[a]
22 593.3185	0.0015	1	1	1	2	1	2	$(6,0)^-2$	
22 595.1003	0.0084	2	2	1	1	1	0	$(7,0)^+0$	[a,b]
22 599.9421	0.0017	5	2	3	4	2	2	$(7,0)^-0$	[a]
22 600.5728	0.0015	5	1	4	4	1	3	$(7,0)^-0$	[a]
22 600.8026	0.0013	6	2	5	5	1	4	$(7,0)^+0$	[a]
22 601.3800	0.0021	2	2	0	1	1	1	$(7,0)^+0$	[a]
22 605.0187	0.0107	6	1	5	5	1	4	$(7,0)^-0$	[a,b]
22 605.6031	0.0042	6	2	4	5	2	3	$(7,0)^-0$	[a,b]
22 606.5691	0.0023	3	2	2	2	1	1	$(7,0)^+0$	[a]
22 609.9781	0.0056	5	2	4	4	1	3	$(7,0)^+0$	[a,b]
22 610.3977	0.0156	4	2	3	3	1	2	$(7,0)^+0$	[a,b]
22 614.2816	0.0012	2	2	0	1	0	1	$(4,2)^-1$	[a]
22 622.7290	0.0011	2	2	0	1	0	1	$(7,0)^-0$	[a]
22 627.2807	0.0044	3	2	1	2	1	2	$(7,0)^+0$	[a,b]
22 628.8083	0.0120	3	3	0	2	2	1	$(7,0)^+0$	[a,b]
22 636.7515	0.0127	4	3	2	3	2	1	$(7,0)^+0$	[a,b]
22 639.6868	0.0035	5	3	3	4	2	2	$(7,0)^+0$	[a,b]
22 644.2991	0.0116	4	4	1	3	3	0	$(7,0)^+0$	[b]
22 650.1270	0.0062	5	5	0	4	4	1	$(7,0)^+0$	[b]
22 651.3529	0.0010	2	2	1	2	2	0	$(6,0)^-2$	[a]
22 652.8079	0.0029	5	4	2	4	3	1	$(7,0)^+0$	
22 653.8481	0.0012	2	2	0	2	2	1	$(6,0)^-2$	[a]
22 654.4493	0.0070	5	4	1	4	3	2	$(7,0)^+0$	[a,b]
22 656.4593	0.0043	6	4	3	5	3	2	$(7,0)^+0$	[a,b]
22 660.9624	0.0050	5	3	2	4	2	3	$(7,0)^+0$	[a,b]
22 664.3027	0.0016	3	1	2	3	0	3	$(6,0)^+2$	[a,b]
22 669.7629	0.0008	2	0	2	1	0	1	$(6,0)^-2$	[a]
22 677.2480	0.0034	4	3	1	3	1	2	$(7,0)^-0$	[a,b]
22 686.1266	0.0016	2	1	1	1	1	0	$(6,0)^-2$	[a]
22 693.6840	0.0008	5	2	3	4	0	4	$(7,0)^-0$	[a]
22 698.5935	0.0030	4	0	4	3	0	3	$(6,0)^-2$	[b]
22 706.7604	0.0010	3	1	2	2	1	1	$(6,0)^-2$	
22 715.8443	0.0011	4	2	3	4	0	4	$(6,0)^-2$	[a]
22 717.4402	0.0018	3	2	2	2	2	1	$(6,0)^-2$	[a]
22 725.3790	0.0011	6	2	4	5	1	5	$(7,0)^+0$	[a]
22 731.6523	0.0018	4	2	3	3	2	2	$(6,0)^-2$	[a]
22 736.1488	0.0024	5	4	2	4	2	3	$(7,0)^-0$	[a]
22 755.6682	0.0008	5	5	1	4	3	2	$(7,0)^-0$	[a]
23 850.7596	0.0013	3	1	3	4	1	4	$(7,0)^-1$	[a]
23 860.9078	0.0016	2	2	0	3	2	1	$(7,0)^-1$	[a]
23 861.4523	0.0012	2	1	1	3	1	2	$(7,0)^-1$	[a]
23 873.1922	0.0022	2	0	2	3	0	3	$(7,0)^-1$	[a]
23 902.2549	0.0016	1	1	1	2	1	2	$(7,0)^-1$	[a]
23 935.1844	0.0012	2	2	1	2	2	0	$(7,0)^-1$	[a]
23 938.1576	0.0024	2	2	0	2	2	1	$(7,0)^-1$	[a,b]
23 939.3805	0.0013	1	1	1	1	1	0	$(7,0)^-1$	[a,b]
23 981.2542	0.0016	2	1	2	1	1	1	$(7,0)^-1$	
23 986.1588	0.0014	2	0	2	1	0	1	$(7,0)^-1$	[a]
23 992.4560	0.0016	2	1	1	1	1	0	$(7,0)^-1$	[a]
23 996.0773	0.0012	3	1	3	2	1	2	$(7,0)^-1$	[a]
24 001.2503	0.0017	2	2	1	2	0	2	$(7,0)^-1$	[a]
24 003.3134	0.0010	3	2	2	2	2	1	$(7,0)^-1$	
24 005.4788	0.0018	4	0	4	3	0	3	$(7,0)^-1$	
24 913.1414	0.0018	6	1	6	7	0	7	$(8,0)^+0$	[a]
24 949.4844	0.0023	5	0	5	6	1	6	$(8,0)^+0$	[a]
24 953.8392	0.0033	4	1	3	5	1	4	$(8,0)^-0$	[a]
24 979.1229	0.0018	3	2	1	4	2	2	$(8,0)^-0$	
24 983.3085	0.0028	4	1	4	5	0	5	$(8,0)^+0$	[b]

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TABLE II. (*Continued*).

ν/cm^{-1}	Int	J''	K_a''	K_c''	J'	K_a'	K_c'	Band	
24 986.8783	0.0018	4	2	3	4	3	2	$(8,0)^+0$	a,b
24 988.8638	0.0045	3	2	2	4	2	3	$(8,0)^-0$	a
24 991.0094	0.0016	3	1	2	4	1	3	$(8,0)^-0$	b
25 000.0821	0.0016	4	2	2	4	3	1	$(8,0)^+0$	
25 009.7843	0.0022	4	0	4	4	2	3	$(8,0)^-0$	a,b
25 011.6134	0.0022	3	0	3	4	1	4	$(8,0)^+0$	
25 015.0147	0.0063	3	1	3	4	1	4	$(8,0)^-0$	b
25 017.3822	0.0031	2	2	0	3	2	1	$(8,0)^-0$	a,b
25 022.2382	0.0024	4	4	0	4	4	1	$(8,0)^-0$	b
25 043.2547	0.0069	2	1	2	3	0	3	$(8,0)^+0$	a,b
25 054.3275	0.0039	3	1	2	3	2	1	$(8,0)^+0$	b
25 062.7781	0.0049	3	3	1	3	3	0	$(8,0)^-0$	b
25 063.1642	0.0024	3	3	0	3	3	1	$(8,0)^-0$	b
25 070.5266	0.0024	1	0	1	2	0	2	$(8,0)^-0$	b
25 077.0840	0.0018	3	2	2	3	2	1	$(8,0)^-0$	a
25 092.1389	0.0029	2	2	1	2	2	0	$(8,0)^-0$	b
25 094.6448	0.0067	2	2	0	2	2	1	$(8,0)^-0$	a,b
25 096.4841	0.0049	0	0	0	1	0	1	$(8,0)^-0$	b
25 117.5098	0.0029	1	1	0	1	1	1	$(8,0)^-0$	
25 131.5763	0.0024	5	1	4	5	1	5	$(8,0)^-0$	
25 142.8786	0.0021	5	2	4	5	0	5	$(8,0)^-0$	
25 154.2984	0.0017	3	2	2	2	2	1	$(8,0)^-0$	a
25 156.2144	0.0042	2	1	2	1	0	1	$(8,0)^+0$	a
25 157.7674	0.0032	5	1	4	4	2	3	$(8,0)^+0$	b
25 161.7007	0.0037	7	1	6	6	2	5	$(8,0)^+0$	
25 162.5304	0.0058	6	1	5	5	2	4	$(8,0)^+0$	b
25 165.4523	0.0035	7	2	6	6	2	5	$(8,0)^-0$	b
25 166.3508	0.0031	3	0	3	2	0	2	$(8,0)^-0$	b
25 169.7733	0.0028	4	0	4	3	1	3	$(8,0)^+0$	b
25 170.3754	0.0036	7	0	7	6	1	6	$(8,0)^+0$	b
25 171.8302	0.0022	5	0	5	4	1	4	$(8,0)^+0$	a
25 172.4958	0.0022	6	0	6	5	1	5	$(8,0)^+0$	
25 174.0285	0.0059	6	1	6	5	0	5	$(8,0)^+0$	a,b
25 174.6946	0.0020	5	1	5	4	0	4	$(8,0)^+0$	
25 179.9438	0.0024	4	1	3	3	1	2	$(8,0)^-0$	a
25 185.9342	0.0039	6	1	5	5	1	4	$(8,0)^-0$	b
25 192.4960	0.0006	5	2	4	4	1	3	$(8,0)^+0$	b
25 194.0657	0.0019	3	2	2	2	1	1	$(8,0)^+0$	
25 196.0385	0.0047	4	2	3	3	1	2	$(8,0)^+0$	a,b
25 212.0501	0.0024	3	3	1	2	2	0	$(8,0)^+0$	
25 219.0955	0.0042	4	3	2	3	2	1	$(8,0)^+0$	b
25 224.8963	0.0028	4	4	1	3	3	0	$(8,0)^+0$	

[a]Assignments confirmed by combination differences.
[b]Transition also observed by Camy-Peyret *et al.* (Ref. 9).

have made assignments which have not been confirmed by combination differences. We are confident that most of these assignments are correct but they cannot be regarded as confirmed.

Also given in Tables III are the errors in our *ab initio* energy levels for each of the observed states. These errors are quite large, up to 10 cm^{-1}, too large for the calculated transition wave numbers to be used for assignments simply by attempting a direct spectral match. However, for a given vibrational band the variation in the error between levels is fairly small, often less than 1 cm^{-1} for the entire band. In this context it should be noted that the energy levels given in Tables III are predicted by the spectroscopically determined PS linelist with errors of 20–150 cm^{-1} and that errors varying by up to 100 cm^{-1} are found within one vibrational band.

The summary Table I also gives band origins for the vibrational states we observe. In three cases, $(7,0)^+0$,

TABLE III. H$_2$ ^{16}O vibration-rotation energy levels in cm^{-1} derived using experimental data. ''o-c'' gives the difference between observed and our *ab initio* prediction. ''N'' gives the number of transitions observed to a particular level, if no number is specified the level is taken from Camy-Peyret *et al.* (Ref. 9).

	$(4,2)^-1$	o-c	N	$(7,0)^-0$	o-c	N	$(7,0)^+0$	o-c	N
0 0 0				22 529.445	5.3		22 529.295	5.0	1
1 0 1				22 550.317	5.2		22 550.183	5.0	2
1 1 1				22 560.267	5.2				
1 1 0				22 565.039			22 564.879		1
2 0 2				22 590.688	5.2		22 589.946	4.7	2
2 1 2				22 597.260	5.3		22 597.128	5.3	
2 1 1	22 601.554	3.7	1	22 611.512	5.2		22 611.328	5.3	2
2 2 1	22 637.077	3.7	2	22 645.806	1.9	3	22 637.471	4.2	2
2 2 0	22 638.071	3.5	4	22 646.514	2.1		22 638.516	4.1	2
3 0 3				22 651.860	5.3	3	22 648.361	4.8	
3 1 3				22 651.958	5.2		22 648.433	5.2	2
3 1 2				22 680.201	4.9		22 679.909	5.1	3
3 2 2	22 713.069	4.6	2	22 700.581	5.5		22 701.787	5.7	2
3 2 1							22 706.707	4.9	2
3 3 1				22 764.558	6.7				
3 3 0				22 764.860	6.7		22 763.710	5.1	2
4 0 4				22 723.717	6.6		22 722.073	3.2	3
4 1 4				22 723.735	6.5	2	22 722.103	3.4	2
4 1 3				22 769.738	6.3		22 769.050	5.1	3
4 2 3							22 783.762	4.7	4
4 2 2	22 796.902	4.2	2	22 804.121	5.0	3			
4 3 2				22 849.044	4.8	3	22 848.907	5.1	2
4 3 1				22 850.604	4.8		22 850.561	5.1	1
4 4 1				22 929.552	5.1	1	22 929.717	5.1	1
4 4 0				22 929.585	5.1	2			
5 0 5				22 812.250	5.6		22 812.171	6.0	2
5 1 5				22 811 510	4.6		22 812.835	6.4	2
5 1 4				22 876.067	4.8	3	22 876.533	5.1	3
5 2 4				22 885.154	5.0	3	22 885.475	5.7	3
5 2 3				22 915.721	4.9	3	22 915.863	5.0	2
5 3 3							22 955.466	5.1	4
5 3 2							22 961.338	5.2	5
5 4 2				23 036.512	5.2	4	23 036.650	5.2	1
5 4 1							23 036.965	5.2	2
5 5 1				22 138.185	5.2	4	23 138 234	5.2	
5 5 0				22 138.185			23 138.234	5.2	1
6 0 6				22 917.405	4.0		22 916.749	4.7	2
6 1 6				22 915.872	5.5	2	22 916.760	5.3	3
6 1 5				23 004.476	4.6		23 004.107	5.2	3
6 2 5				23 000.561	5.4	3	23 000.260	5.0	3
6 2 4				23 052.082	5.7	2	23 052.004	5.0	3
6 3 4							23 056.857	5.6	2
6 3 3									
6 4 3							23 165.271	5.2	3
7 0 7							23 038.351	5.9	1
7 1 7				23 037.857	6.0	1			
7 1 6							23 140.406	6.1	1
8 0 8									
8 1 8							23 175.157	6.1	2

	$(6,0)^+2$	o-c	N	$(6,0)^-2$	o-c	N	$(7,0)^-1$	o-c	N
0 0 0									
1 0 1									
1 1 1				22 672.814	3.1	1	23 981.751	3.4	2
1 1 0									
2 0 2				22 693.593	2.8	2	24 009.953	2.8	2
2 1 2	22 709.423	3.2	3				24 018.391	3.6	1
2 1 1				22 728.515	3.3	2	24 034.817	3.0	2
2 2 1				22 787.516	6.3	2	24 071.348	3.1	2
2 2 0				22 788.749	6.7	2	24 073.059	3.2	2
3 0 3	22 754.044	3.2	1						
3 1 3				22 765.082	3.2	1	24 075.573	2.0	2
3 1 2	22 801.070	3.2	2	22 801.936	3.6	1			

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TABLE III. (Continued).

3 2 2	22 852.342	6.0	2	24 138.215	5.7	1
4 0 4	22 835.355	3.7	1	24 142.240	2.0	1
4 1 4						
4 1 3						
4 2 3	22 937.953	6.2	2			

	$(8,0)^-0$	o-c	N	$(8,0)^+0$	o-c	N
0 0 0	25 120.278	8.3	1			
1 0 1	25 140.617	8.3	1			
1 1 1	25 150.149	7.9				
1 1 0	25 154.646		1			
2 0 2	25 180.795	9.0				
2 1 2				25 180.008	1.9	2
2 1 1	25 199.784	8.3				
2 2 1	25 228.302	8.3	1			
2 2 0	25 229.546	8.3	2			
3 0 3	25 236.441	8.2	1	25 236.451	8.2	1
3 1 3	25 239.852	8.3	1			
3 1 2	25 266.476	8.4	1	25 266.483	8.0	1
3 2 2	25 289.200	8.0	3	25 289.241	8.3	1
3 2 1	25 294.902	8.0	1			
3 3 1	25 348.582	8.6	1	25 348.214	8.3	1
3 3 0	25 348.383	8.2	1			
4 0 4	25 310.132	8.0		25 312.051	9.9	1
4 1 4				25 308.656	8.0	1
4 1 3	25 353.309	8.0	2			
4 2 3				25 369.403	8.0	2
4 2 2				25 383.924	8.0	1
4 3 2				25 431.251	8.0	1
4 3 1						
4 4 1				25 510.288	8.0	1
4 4 0	25 510.345	8.0	1			
5 0 5				25 396.736	8.0	2
5 1 5	25 396.105	7.9		25 396.747	8.0	1
5 1 4	25 458.201	8.1	1	25 458.129	8.0	1
5 2 4	25 468.226	8.2	1	25 467.993	8.1	1
6 0 6				25 499.121	8.0	1
6 1 6				25 499.376	7.9	2
6 1 5	25 585.391	8.8	1	25 578.739	7.7	1
7 0 7				25 617.627	8.0	1
7 1 7						
7 1 6				25 714.612	8.1	1
7 2 6	25 718.363	9.4	1			

$(7,0)^-0$, and $(8,0)^-0$, accurate values are given for the band origins as the 0_{00} level has been observed for these states. For the other vibrational states the 0_{00} has yet to be observed and the vibrational band origins have been estimated from the *ab initio* values corrected by the average band errors. We expect this procedure to give values accurate to ± 1 cm^{-1}. Indeed our previous predictions made in this fashion have proved remarkably accurate, see I.

The 242 transitions assigned here, when combined with the 59 previously assigned by Camy-Peyret *et al.*,[9] mean that over half the transitions we observe in the near-ultraviolet have been assigned. However, the pattern of these assignments is not uniform. In regions where we have successfully identified a vibrational band, most (about 80%) of transitions have been assigned. However we have some large regions in which we have made no assignments. For example, there are 38 unassigned lines in the 21 430–22 240 cm^{-1} region and 32 unassigned lines in the 22 756–23 845 cm^{-1} region. All of these lines are weak and their sparseness makes them hard to analyze with our procedure.

At high wave numbers we observe an increasing discrepancy between our calculated intensities and the measured ones. This problem appears to be caused by our choice of dipole surface and is currently being investigated.

V. CONCLUSIONS

A newly recorded, long pathlength, room temperature, rotation-vibration spectrum of water in the near-ultraviolet has been presented. This spectrum has been analyzed using a newly computed *ab initio* linelist. As a result, five new vibrational bands of water have been observed for the first time. One of each of these new states belongs to the previously unobserved $6\nu + \delta$ and $7\nu + \delta$ polyads, two belong to the 7ν polyad, and one to the 8ν polyad. However, it should be noted that according to the analysis of Rose and Kellman,[11] the polyad structure of water has started breaking down in the energy region studied here.

We anticipate that our new data will be of interest for scientists working on atmospheric studies, which usually neglect many of the weak lines of water because they are poorly characterized and difficult to analyze. Furthermore, the high-lying energy levels obtained here are important input data for assessing and refining (effective) potential energy surfaces for water which, in turn, can themselves be used for further spectroscopic analysis.

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