THE ASTROPHYSICAL JOURNAL, 379:L41–L43, 1991 September 20

MILLIMETER- AND SUBMILLIMETER-WAVE SPECTRUM OF HIGHLY EXCITED STATES OF WATER

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Received 1991 June 13; accepted 1991 July 10

ABSTRACT

To facilitate studies of water in the interstellar medium and late-type stars, we have measured the frequencies of 30 new millimeter- and submillimeter-wave transitions of $H_2{}^{16}O$ which lie between 100 GHz and 600 GHz. This represents almost a doubling of the number of water lines that have been observed in the laboratory in this spectral region at high resolution. All of the newly observed lines are highly excited, lying between 2400 and 4200 cm^{-1} above the ground level. Some of these have large excitation energies because of their high rotational states and others because they lie in excited vibrational states. These lines are potentially of substantial astrophysical significance because they are related to the study of interstellar masers and because their high excitation eliminates the atmospheric self-absorption associated with the more well-known water lines.

Subject headings: interstellar: molecules — laboratory spectra — line identifications — molecular processes

1. INTRODUCTION

The observation of water in extraterrestrial sources has always posed a major experimental challenge because of the abundance of water in Earth's atmosphere and the paucity of millimeter-wave transition frequencies. In spite of this, water can be observed astronomically because it is one of the most abundant interstellar species (at least in star formation regions), because of its strong spectral features, and because it is often detected as a maser. The well-known $6_{1,6}$–$5_{2,3}$ transition at 22 GHz (which is the major contributor to atmospheric opacity in the microwave region) has been observed extensively from the ground, partly because its relatively high energy levels ($\sim$640 K or 447 cm^{-1}) result in a weaker interfering atmospheric feature relative to the signals emanating from hotter astronomical sources. This is also true for the $5_{1,5}$–$4_{2,2}$ transition at 325 GHz, with an excitation of 327 cm^{-1}, which has only recently been detected as a maser from the ground (Menten et al. 1990b). In addition, the $3_{1,3}$–$2_{2,0}$ transition at 183 GHz and the $4_{1,4}$–$3_{2,1}$ transition at 380 GHz have been observed (Waters et al. 1980; Phillips, Kwan, & Huggins 1980), albeit from aircraft, since they are relatively low lying—142 cm^{-1} and 225 cm^{-1}, respectively. The former transition has now also been seen from the ground in exceptionally good weather (Cernicharo et al. 1990). Transitions of the singly deuterated isotopomer HDO have also been reported (Moore, Langer, & Huguenin 1986; Jacq et al. 1990), with a recent sighting of the fundamental $1_{0,1}$–$0_{0,0}$ transition at 465 GHz from the ground (Schulz et al. 1991). The low-lying $1_{1,0}$–$1_{0,1}$ 548 GHz transition of $H_2{}^{18}O$ has been searched for from aircraft unsuccessfully (Wannier et al. 1991) although a higher lying transition has been detected from the ground (Jacq et al. 1990).

More recently, observations have been made which provide a new and interesting approach to the observation of water—the ground-based detection of transitions between highly excited energy levels. This is especially significant because it enhances the observations of stellar atmospheres and active regions of star formation, and probes those levels closely associated with maser action. In the first such observation, Menten & Melnick (1989), using the IRAM telescope, reported observation of the $4_{4,0}$–$5_{3,3}$ transition at 96 GHz and the $5_{5,0}$–$6_{4,3}$ transition at 233 GHz in the ν_2 excited vibrational state toward the supergiant VY CMa, with the latter transition also detected toward W Hya. These transitions have upper levels at 2130 and 2406 cm^{-1}, respectively. In addition, Menten, Melnick, & Phillips (1990a) and Menten & Melnick (1991) observed probable maser action in the rotationally highly excited (1294 cm^{-1}) $10_{2,9}$–$9_{3,6}$ transition at 321 GHz in the ground vibrational state toward both star formation regions and late-type stars, using the Caltech Submillimeter Observatory. These successes show that a significant opportunity for similar measurements based on other highly excited water lines exists (Menten 1990, 1991).

Water is the major contributor to atmospheric opacity at microwave, millimeter-wave, and far-infrared wavelengths. As a result, its spectrum in these regions has been the subject of extensive experimental and theoretical investigation and in many respects can be considered as being well characterized. However, there is an important and astronomically significant exception to this. Many astronomical sources are significantly hotter than Earth's atmosphere. As a result, many transitions which are strong in the sense that they are strongly allowed have vanishingly small contributions to the atmosphere's opacity while at the same time being significant astronomical sources from hot regions. In general, the frequencies of these lines are not well known because their high excitation makes experimental measurements difficult and theoretical extrapolations uncertain. Despite these problems, further observational studies of highly excited water require additional laboratory work. In this *Letter*, we address this issue and report a laboratory study of many highly excited lines of water of astrophysical interest in the millimeter- and submillimeter-wave spectral region.

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2. LABORATORY SPECTROSCOPY

Water has always been one of the most studied molecular species because of its ubiquity in nature, its influence on atmospheric propagation, and its position as a prototype of an important spectroscopic family, the light asymmetric rotor. Recently, this last role for water has been extensively investigated, both in its pure rotational spectrum in the microwave through the far infrared (De Lucia et al. 1972; Messer, De Lucia, & Helminger 1984) and its rotation-vibration spectrum in the infrared (Camy-Peyret et al. 1977).

Unfortunately, the theoretical characterization of the spectrum of water is not straightforward. The enormously successful Hamiltonian of Watson (1966), which has been used to characterize the spectra of so many species, converges very slowly because of the extreme effects of centrifugal distortion in water. Furthermore, the 100, 020, and 001 excited vibrational states (where the three numbers refer to $v_1 v_2 v_3$, respectively) interact with one another, further complicating the analysis. As a consequence, it is difficult to use theoretical methods to predict accurately unobserved water features. This is especially true for the highly excited lines which are the subject of this *Letter*.

We have described previously the general experimental and theoretical techniques used to study the millimeter- and submillimeter-wave spectrum of water in the laboratory (Helminger, De Lucia, & Gordy 1970; De Lucia et al. 1972; Messer et al. 1984). For this work, we have used a hot cell, 5 cm in diameter and 1.5 m long, which can be heated to ~1400 K with electric resistance heaters. In order to minimize the possibilities of impurity outgassing at high temperature, the cell was continuously pumped with a diffusion pump and the water sample continuously replenished to provide a typical sample pressure of 100 mTorr.

Because of the slow convergence of the Hamiltonian, initial searches were based primarily on energy levels derived from infrared studies (Flaud & Camy-Peyret 1974; Flaud, Camy-Peyret, & Maillard 1976; Camy-Peyret et al. 1977). However, the expected (and observed) accuracy of these predictions varies according to the origin of the excitation energy. In those cases where much of the excitation energy comes from the energy of the vibrational state which contains the observed rotational transition (e.g., the $1_{1,0}$–$1_{0,1}$ rotational transition in the 100 vibrational state), the predictions are good because these are related to strong infrared lines with origins in well-

TABLE 1

MICROWAVE $H_2{}^{16}O$ ROTATIONAL TRANSITIONS

$J'K_a'K_c'$ – $J''K_a''K_c''$	$v_1v_2v_3$	Frequency (MHz)	Upper Energy[a] (cm^{-1})	Ref.
1 1 0 - 1 0 1	0 0 0	556936.002	42.37	b,c
2 0 2 - 1 1 1	0 0 0	987926.764	70.09	d
2 1 1 - 2 0 2	0 0 0	752033.227	95.18	c
3 1 3 - 2 2 0	0 0 0	183310.117	142.28	e,f
4 1 4 - 3 2 1	0 0 0	380197.372	224.84	c,g
4 2 2 - 3 3 1	0 0 0	916171.582	315.78	d
4 2 3 - 3 3 0	0 0 0	448001.075	300.36	c,g
5 1 5 - 4 2 2	0 0 0	325152.919	326.63	c,g
5 2 4 - 4 3 1	0 0 0	970315.022	416.21	d
5 3 2 - 4 4 1	0 0 0	620700.807	508.81	c
5 3 3 - 4 4 0	0 0 0	474689.127	503.97	c
6 1 6 - 5 2 3	0 0 0	22235.080	447.25	h,i
6 4 2 - 5 5 1	0 0 0	470888.947	757.78	c
6 4 3 - 5 5 0	0 0 0	439150.812	756.72	c
6 2 4 - 7 1 7	0 0 0	488491.133	602.77	c
7 5 2 - 6 6 1	0 0 0	443018.295	1059.84	c
7 5 3 - 6 6 0	0 0 0	437346.667	1059.65	c
8 6 2 - 7 7 1	0 0 0	504482.692	1411.65	d,j
8 6 3 - 7 7 0	0 0 0	503568.532	1411.61	d,j
9 7 2 - 8 8 1	0 0 0	645905.620	1810.59	j
9 7 3 - 8 8 0	0 0 0	645766.010	1810.58	j
10 2 9 - 9 3 6	0 0 0	321225.640	1293.63	c
10 3 7 -11 2 10	0 0 0	390134.508	1538.15	d
12 6 7 -13 3 10	0 0 0	571913.580	2433.80	k
13 6 8 -14 3 11	0 0 0	259952.444	2748.11	l
14 3 12 -13 4 9	0 0 0	530342.860	2551.49	k
14 6 9 -15 3 12	0 0 0	139614.293	3084.84	l
14 4 10 -15 3 13	0 0 0	247440.096	2880.83	l
15 6 10 -16 3 13	0 0 0	177317.068	3443.21	l
16 6 11 -17 3 14	0 0 0	339043.996	3822.25	l
17 4 13 -16 7 10	0 0 0	354808.877	4017.91	l
1 1 0 - 1 0 1	0 1 0	658006.550	1640.51	d
2 2 0 - 3 1 3	0 1 0	119995.940	1743.49	m
4 2 3 - 3 3 0	0 1 0	12008.800	1908.02	m
4 1 4 - 3 2 1	0 1 0	67803.960	1821.60	n
4 2 2 - 3 3 1	0 1 0	463170.460	1922.09	o,k
4 2 2 - 5 1 5	0 1 0	2159.980	1922.09	p
5 3 2 - 4 4 1	0 1 0	26834.270	2130.49	m
4 4 0 - 5 3 3	0 1 0	96261.160	2129.62	m
5 2 4 - 4 3 1	0 1 0	546690.600	2024.15	o
5 5 0 - 6 4 3	0 1 0	232686.700	2406.14	o
5 5 1 - 6 4 2	0 1 0	209118.370	2406.14	l
5 2 3 - 6 1 6	0 1 0	336227.620	2053.97	o
6 3 4 - 5 4 1	0 1 0	595079.800	2271.17	o
6 6 1 - 7 5 2	0 1 0	293664.442	2733.96	l
6 6 0 - 7 5 3	0 1 0	297439.107	2733.96	l
7 4 4 - 6 5 1	0 1 0	498502.590	2569.51	k
7 4 3 - 6 5 2	0 1 0	578057.486	2572.14	l
7 7 0 - 8 6 3	0 1 0	263451.357	3109.91	l
7 7 1 - 8 6 2	0 1 0	262897.748	3109.91	l
8 5 3 - 7 6 2	0 1 0	440736.910	2920.13	k
8 5 4 - 7 6 1	0 1 0	425689.190	2919.63	k
9 2 8 - 8 3 5	0 1 0	593708.497	2690.60	l
9 6 3 - 8 7 2	0 1 0	441238.866	3321.01	l
9 6 4 - 8 7 1	0 1 0	438724.178	3320.93	l
10 7 4 - 9 8 1	0 1 0	548474.403	3770.71	l
14 3 12 -13 4 9	0 1 0	323554.019	4184.84	l
3 2 1 - 4 1 4	0 2 0	331123.815	3392.74	l
4 2 2 - 5 1 5	0 2 0	403492.421	3495.93	l
6 2 5 - 5 3 2	0 2 0	402914.594	3736.16	l
6 5 2 - 7 4 3	0 2 0	268149.117	4197.33	l
6 5 1 - 7 4 4	0 2 0	323524.781	4197.36	l
7 3 5 - 6 4 2	0 2 0	526487.143	4033.62	l
1 1 0 - 1 0 1	1 0 0	540754.189	3698.49	l
3 1 3 - 2 2 0	1 0 0	196973.966	3796.54	l
4 1 4 - 3 2 1	1 0 0	384076.969	3877.58	l
4 2 3 - 3 3 0	1 0 0	478778.912	3951.32	l
5 1 5 - 4 2 2	1 0 0	326687.287	3977.46	l
1 1 0 - 1 0 1	0 0 1	524292.891	3796.98	l
5 1 5 - 4 2 2	0 0 1	322975.057	4076.90	l

[a] Energy levels taken from Camy-Peyret et al. 1977; Flaud & Camy-Peyret 1974; Flaud et al. 1976.

REFERENCES.—(b) Stephenson & Strauch 1970; (c) De Lucia et al. 1972; (d) Helminger et al. 1983; (e) King & Gordy 1954; (f) Winton 1972; (g) Lichenstein et al. 1966; (h) Becker & Autler 1946; (i) Kukolich 1969; (j) Burenin et al. 1983; (k) Baskakov et al. 1987; (l) this work; (m) Kuze 1980; (n) Steenbeckliers & Bellet 1971; (o) Belov et al. 1987; (p) Herman et al. 1979.

populated rotational levels of the ground vibrational state. On the other hand, lines which are highly excited because of high-lying rotational energy (e.g., the $17_{4,13}$–$16_{7,10}$ rotational transition in the 000 [ground] vibrational state) have their origins in weakly populated rotational levels, are related to lines with weak infrared spectra, and are generally more poorly predicted.

3. RESULTS

Table 1 shows the results of our work as well as all other previously measured millimeter- and submillimeter-wave water lines in the literature of which we are aware. Typical measurement uncertainty is about 100 kHz. An important issue is the certainty of the assignments. Fortunately, water is a species with a sparse spectrum, and the lines listed in the tables represent essentially all of the strongest lines in the spectral regions considered here.

However, there are two major remaining concerns. First, all of our measurements were made with a harmonic generation technique which generates multiple harmonics simultaneously. As a result, all identifications have been checked to see if the observed line is alternatively assignable to another line in another harmonic.

The second concern is that of impurities. Some of the observed lines are rather weak because of their high excitation, and many species which might be impurities have very strong spectra. This is always a concern in spectroscopy, and the usual guard against it is an overdetermined theoretical model capable of predicting any one measurement on the basis of the others to near the accuracy of the measurement itself. Unfortunately, the model for some of the highly excited states reported here is not this good. However, a slightly weaker version of the same statistical argument still exists. In all cases the searches were started at the frequency calculated from the infrared energy levels and expanded outward. In no cases did we have more than one line to choose from, and in all cases the intensities of the observed lines were consistent with our expectations to about a factor of 2 out of a dynamic range for the system of about 10^5. In addition, the absorptivity as a function of temperature for a highly excited line is a very steep and well-known function of temperature, although the long thermal time constant of the cell prevented our taking full advantage of this signature. Of the lines reported in Table 1, the assignments of the $10_{7,4}$–$9_{8,1}$ and $14_{3,12}$–$13_{4,9}$ transitions in the 010 vibrational state are probably the least certain because their quantum states are least like those of the other observed states, thereby making the fitting/extrapolation procedure most difficult.

Note added in manuscript.—After submission of this manuscript, we learned of a manuscript (Amano & Scappini 1991) in which the study of four rotationally excited lines of the ground vibrational state of water plus one line of the $2\nu_2$ (020) state was reported. The agreement between their results and ours is satisfactory, with differences in reported frequencies ranging from fewer than 10 kHz to a maximum of 300 kHz.

This work was supported by the National Aeronautics and Space Administration via grant NAGW-1259.

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