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CALCULATED ROTATIONAL AND ROVIBRATIONAL TRANSITIONS IN THE SPECTRUM OF H_3^+

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ABSTRACT

New calculations of line strengths and transition frequencies for the "forbidden" rotational spectrum and the ν_2 fundamental rovibrational band of H_3^+ are presented. These first principles calculations use the highly accurate ab initio electronic potential energy surface of Meyer, Botschwina, and Burton, which has previously been shown by the authors to give rovibrational transition frequencies, rotational constants and vibrational fundamentals of spectroscopic accuracy. The line strengths calculated for the pure rotational spectrum in the vibrational ground state are in general agreement with those previously predicted by Pan and Oka, although individual line strengths may differ by as much as 50%. The data are presented to assist with the interstellar detection of this astrophysically important molecular ion.

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

I. INTRODUCTION

The simple molecular ion H_3^+ plays a crucial role (Herbst and Klemperer 1973; Suzuki 1979; van Dishoeck 1986) in ion-molecule reaction schemes for the production of interstellar molecules. Its infrared spectrum has been known from laboratory experiments since 1980 (Oka 1980), and previous calculations have predicted the column density of H_3^+ to be similar to that of HCO^+ (10^{14} cm^{-2}) in dense interstellar clouds (de Jong, Dalgarno and Boland 1983). To date, however, attempts to detect H_3^+ spectroscopically in the interstellar medium have proved unsuccessful (Oka 1981; Burton, von Nagy-Felsobuki, and Smith 1983), although a tentative observation of H_2D^+ has been made (Phillips *et al.* 1985).

In his 1981 search, Oka attempted to observe ν_2 rovibrational transitions, in absorption from the vibrational ground state, in the Orion Molecular Cloud and other locations where, he argued, suitable infrared sources co-existed with sufficient densities of H_3^+. He used laboratory plasma measurements of the ν_2 spectrum which gave accurate transition frequencies. However, it is difficult to extract information about line strengths of the individual transitions from these experiments.

The search for interstellar H_3^+ has also been hampered by the absence of an allowed pure rotational spectrum in the vibrational ground state, since the molecule has no permanent dipole moment. Instead, Pan and Oka (1986) have suggested that it might be possible to observe the "forbidden" rotational spectrum resulting from centrifugal distortions of the molecule due to rotation about the C_2 axes. To this end, they calculated transition dipole moments from the perturbation theory developed by Watson (1971).

Pan and Oka derived their ground state pure rotational transition frequencies from rotational constants calculated from data obtained for the ν_2 spectrum for angular momentum states with $J \leq 4$ (Watson *et al.* 1984). Since then, Majewski *et al.* (1987) have shown that these constants need to be modified for higher angular momentum states. Together with the truncation of the Hamiltonian used for the rotational energies, this means there are significant errors in the transition frequencies Pan and Oka calculated for the higher angular momentum states.

It is possible, however, to obtain energy levels, transition frequencies and line strengths directly from electronic potential energy surfaces calculated ab initio, without recourse to phenomenological theories (Tennyson 1986*a*).

For H_3^+, Meyer, Botschwina, and Burton (1986, hereafter MBB) have specifically designed a surface to give very good agreement with experiment for the vibrational band origins. We have recently used this surface to carry out calculations of the rovibrational energy levels which are of spectroscopic quality (Miller and Tennyson 1987, 1988). Rotational constants calculated for the ground vibrational state and ν_2 fundamental were in excellent agreement with experiment, and frequencies were predicted for "hot band" transitions.

In this paper we have extended the calculation of energy levels to include those angular momentum states considered by Pan and Oka and present what should be the most accurate estimates of line strengths currently available.

II. COMPUTATIONAL DETAILS

Rovibrational energy levels and wave functions were calculated using the corrected MP-7/87CGTO MBB potential (Meyer *et al.* 1986) and the two-step variational method described previously (Sutcliffe, Miller, and Tennyson 1988). The programs SELECT, TRIATOM, and ROTLEV (Tennyson 1986) have been updated to give output which drives a new program DIPOLE (Tennyson and Miller 1988) which calculates transition dipole moments, line strengths, and Einstein A coefficients, the theory of which can be found elsewhere (Brocks, Tennyson, and van der Avoird 1984; Miller *et al.* 1988). Transition dipole moments were also calculated using the dipole surface given by MBB.

Briefly, this method calculates energy levels, wave functions and transition dipole moments directly from the potential energy and dipole surfaces given by ab initio calculations. In addition, no assumptions are made about the equilibrium geometry of the molecule or limiting the internal motions considered to "small" displacements from such an equilibrium. This is extremely important for a molecule like H_3^+, which is known to be very "floppy" and to execute large amplitude

TABLE 1

PURE ROTATIONAL TRANSITIONS FOR H_3^+ IN THE GROUND STATE[a]

JK–$J''K''$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	M_{if} (debye)	$S(f-i)$ (debye)	A_{if} s^{-1}
4 4 3 1	501.875	494.606	7.269	0.144(−1)	0.207(−3)	0.250(−7)
7 6 6 3	1586.082	1576.835	9.247	0.613(−1)	0.376(−2)	0.933(−6)
7 4 8 7	2001.833	1977.171	29.662	0.811(−1)	0.658(−2)	0.538(−4)
4 2 5 5	768.225	728.777	39.444	0.226(−1)	0.512(−3)	0.986(−5)
6 5 5 2	1238.051	1186.725	51.326	0.443(−1)	0.196(−2)	0.830(−4)
8 1 8 2	2924.537	2868.013	56.525	0.134(+0)	0.179(−1)	0.101(−2)
7 1 7 2	2300.153	2241.303	58.850	0.992(−1)	0.985(−2)	0.629(−3)
6 1 6 2	1740.351	1679.265	61.086	0.699(−1)	0.488(−2)	0.349(−3)
5 1 5 2	1249.910	1186.725	63.185	0.460(−1)	0.212(−2)	0.168(−3)
4 1 4 2	833.311	768.225	65.086	0.275(−1)	0.756(−3)	0.654(−4)
3 1 3 2	494.606	427.881	66.725	0.141(−1)	0.200(−3)	0.185(−4)
2 1 2 2	237.279	169.246	68.033	0.537(−2)	0.287(−4)	0.283(−5)
5 3 6 6	1080.139	995.553	84.586	0.324(−1)	0.105(−2)	0.199(−3)
5 4 4 1	928.672	833.311	95.361	0.296(−1)	0.875(−3)	0.238(−3)
8 6 7 3	2241.496	2141.437	100.059	0.944(−1)	0.891(−2)	0.280(−2)
2 2 1 1	169.246	64.104	105.141	0.242(−2)	0.584(−5)	0.213(−5)
6 4 7 7	1430.258	1301.722	128.537	0.438(−1)	0.192(−2)	0.128(−2)
7 5 6 2	1817.565	1679.265	138.301	0.699(−1)	0.489(−2)	0.405(−2)
4 3 3 0	658.503	516.713	141.790	0.245(−1)	0.600(−3)	0.537(−3)
7 5 8 8	1817.565	1646.732	170.384	0.571(−1)	0.326(−2)	0.510(−2)
7 0 7 3	3319.685	2141.437	178.247	0.134(+0)	0.179(−1)	0.319(−1)
6 4 5 1	1430.258	1249.910	180.348	0.487(−1)	0.237(−2)	0.437(−2)
3 2 2 1	427.881	237.279	190.602	0.754(−2)	0.568(−4)	0.123(−3)
5 0 5 3	1270.862	1080.139	190.723	0.586(−1)	0.344(−2)	0.748(−2)
3 0 3 3	516.713	315.248	201.465	0.142(−1)	0.202(−3)	0.518(−3)
8 5 7 2	2462.117	2241.303	220.814	0.998(−1)	0.996(−2)	0.336(−1)
7 4 6 1	2001.833	1740.351	261.482	0.719(−1)	0.516(−2)	0.290(−1)
8 1 8 4	2924.537	2638.339	286.198	0.121(+0)	0.147(−1)	0.108(+0)
7 1 7 4	2300.153	2001.833	298.320	0.854(−1)	0.730(−2)	0.607(−1)
6 3 5 0	1576.835	1270.862	305.972	0.679(−1)	0.460(−2)	0.414(−1)
6 1 6 4	1740.351	1430.258	310.093	0.559(−1)	0.313(−2)	0.293(−1)
5 1 5 4	1249.910	928.672	321.238	0.326(−1)	0.106(−2)	0.110(−4)
3 1 2 2	494.606	169.246	325.360	0.477(−2)	0.288(−4)	0.246(−3)
4 1 4 4	833.311	501.875	331.436	0.149(−1)	0.221(−3)	0.253(−2)
8 4 7 1	2638.339	2300.153	338.186	0.992(−1)	0.984(−2)	0.119(+0)
5 2 4 1	1186.725	833.311	353.414	0.278(−1)	0.770(−3)	0.107(−1)
4 1 3 2	833.311	427.881	405.430	0.118(−1)	0.139(−3)	0.291(−2)
8 2 8 5	2868.013	2462.117	405.896	0.106(+0)	0.112(−1)	0.235(+0)
7 2 7 5	2241.303	1817.565	423.737	0.709(−1)	0.503(−2)	0.120(+0)
6 2 5 1	1679.265	1249.910	429.354	0.435(−1)	0.189(−2)	0.470(−1)
6 2 6 5	1679.265	1238.051	441.213	0.423(−1)	0.179(−1)	0.483(−1)
8 3 7 0	3319.685	2774.839	455.154	0.134(+0)	0.181(−1)	0.535(+0)
5 2 5 5	1186.725	728.777	457.948	0.199(−1)	0.396(−3)	0.119(−1)
5 1 4 2	1249.910	768.225	481.685	0.222(−1)	0.493(−3)	0.173(−1)
7 2 6 1	2241.303	1740.351	500.952	0.633(−1)	0.400(−2)	0.158(+0)
8 3 8 6	2774.839	2241.496	533.342	0.864(−1)	0.746(−2)	0.355(+0)
6 1 5 2	1740.351	1186.725	553.625	0.362(−1)	0.131(−2)	0.698(−1)
7 3 7 6	2141.437	1586.082	555.355	0.526(−1)	0.277(−2)	0.149(+0)
8 2 7 1	2868.013	2300.153	567.860	0.877(−1)	0.769(−2)	0.441(+0)
6 3 6 6	1576.835	995.553	581.281	0.252(−1)	0.633(−3)	0.390(−1)
5 0 4 3	1270.862	658.503	612.359	0.215(−1)	0.463(−3)	0.333(−1)
7 1 6 2	2300.153	1679.265	620.888	0.543(−1)	0.294(−2)	0.221(+0)
8 4 8 7	2638.339	1972.171	666.168	0.634(−1)	0.402(−2)	0.372(+0)
8 1 7 2	2924.537	2241.303	683.235	0.765(−1)	0.585(−2)	0.585(+0)
7 4 7 7	2001.833	1301.722	700.111	0.308(−1)	0.947(−3)	0.102(+0)
7 0 6 3	2319.685	1576.835	742.850	0.615(−1)	0.379(−2)	0.487(+0)
5 1 4 4	1249.910	501.875	748.035	0.793(−2)	0.629(−4)	0.826(−2)
6 1 5 4	1740.351	928.672	811.679	0.181(−1)	0.327(−3)	0.549(−1)
8 5 8 8	2462.117	1646.732	815.835	0.368(−1)	0.135(−2)	0.230(+0)
7 1 6 4	2300.153	1430.258	869.895	0.320(−1)	0.102(−2)	0.211(+0)
8 1 7 4	2924.537	2001.833	922.705	0.497(−1)	0.247(−2)	0.608(+0)
6 2 5 5	1679.265	728.777	950.487	0.918(−2)	0.842(−2)	0.227(−1)
7 2 6 5	2241.303	1238.051	1003.252	0.207(−1)	0.427(−3)	0.135(+0)
8 2 7 5	2868.013	1817.565	1050.447	0.361(−1)	0.130(−2)	0.437(+0)
7 3 6 6	2141.437	995.553	1145.884	0.103(−1)	0.106(−3)	0.501(−1)
8 3 7 6	2774.839	1586.082	1188.757	0.229(−1)	0.525(−3)	0.277(+0)
8 4 7 7	2638.339	1301.722	1336.617	0.113(−1)	0.127(−3)	0.953(−1)

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[a] Powers of 10 in brackets.

TABLE 2

DIPOLE-ALLOWED ROVIBRATIONAL TRANSITIONS FOR H_3^+ IN THE ν_2 FUNDAMENTAL[a]

$J'G'_U$–$J''K''$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	ω_{if}(exp)[b] (cm^{-1})	$S(f-i)$ ($debye^2$)	A_{if} s^{-1}
4 3_{-1} 5 3...........	3144.790	1080.139	2064.651	N.O.[c]	0.330(−2)	0.910(+1)
4 2_{-1} 5 2...........	3259.663	1186.725	2072.938	N.O.	0.383(−2)	0.107(+2)
4 1_{-1} 5 1...........	3325.518	1249.910	2075.608	N.O.	0.132(−2)	0.369(+1)
4 5_{+1} 5 5...........	2863.711	728.777	2134.934	2134.922	0.238(+0)	0.727(+3)
4 4_{+1} 5 4...........	3069.003	928.672	2140.331	2140.348	0.190(+0)	0.583(+3)
4 3_{+1} 5 3...........	3233.027	1080.139	2152.888	2152.887	0.151(+3)	0.472(+3)
3 2_{-1} 4 2...........	2930.998	768.225	2162.773	N.O.	0.121(−2)	0.383(+1)
4 2_{+1} 5 2...........	3351.023	1186.725	2164.298	2164.278	0.126(+0)	0.400(+3)
3 1_{-1} 4 1...........	3002.486	833.311	2169.175	N.O.	0.776(−3)	0.249(+1)
4 1_{+1} 5 1...........	3422.758	1249.910	2172.847	2172.815	0.114(+0)	0.366(+3)
4 0_{-1} 5 0...........	3446.685	1270.862	2175.822	2175.780	0.110(+0)	0.357(+3)
3 4_{+1} 4 4...........	2719.308	501.875	2217.434	2217.451	0.184(+0)	0.628(+3)
3 3_{+1} 4 3...........	2876.591	658.503	2218.088	2218.129	0.137(+0)	0.469(+3)
3 2_{+1} 4 2...........	2992.161	768.225	2223.936	2223.965	0.104(+0)	0.359(+3)
3 1_{+1} 4 1...........	3063.193	833.311	2229.881	2229.895	0.857(−1)	0.298(+3)
2 1_{-1} 3 1...........	2755.291	494.606	2260.685	N.O.	0.551(−4)	0.200(+0)
2 1_{+1} 3 1...........	2790.127	494.606	2295.521	2295.577	0.607(−1)	0.230(+3)
2 2_{+1} 3 2...........	2723.765	427.881	2295.884	2295.947	0.864(−1)	0.328(+3)
2 0_{-1} 3 0...........	2812.642	516.713	2295.930	2295.980	0.523(−1)	0.198(+3)
2 3_{+1} 3 3...........	2614.135	315.248	2298.887	2298.930	0.130(+0)	0.496(+3)
1 1_{+1} 2 1...........	2609.377	237.279	2371.099	2372.185	0.386(−1)	0.162(+3)
1 2_{+1} 2 2...........	2548.041	169.246	2378.795	2378.869	0.775(−1)	0.327(+3)
0 1_{+1} 1 1...........	2521.282	64.104	2457.178	2457.290	0.257(−1)	0.119(+3)
5 4_{-1} 5 4...........	3395.911	928.672	2467.239	N.O.	0.865(−1)	0.407(+3)
5 0_{-1} 5 0...........	3742.346	1270.862	2471.483	2471.210	0.264(+0)	0.125(+4)
5 1_{-1} 5 1...........	3721.811	1249.910	2471.901	2472.325	0.254(+0)	0.120(+4)
5 3_{-1} 5 3...........	3552.620	1080.139	2472.481	2472.846	0.168(+0)	0.796(+3)
5 2_{-1} 5 2...........	3659.563	1186.725	2472.838	2473.238	0.222(+0)	0.105(+4)
4 3_{-1} 4 3...........	3144.790	658.503	2486.287	2486.559	0.855(−1)	0.412(+3)
4 2_{-1} 4 2...........	3259.663	768.225	2491.438	2491.749	0.162(+0)	0.784(+3)
4 1_{-1} 4 1...........	3325.518	833.311	2492.207	2492.541	0.206(+0)	0.100(+4)
3 2_{-1} 3 2...........	2930.998	427.881	2503.117	2503.347	0.850(−1)	0.418(+3)
3 1_{-1} 3 1...........	3002.486	494.606	2507.880	2508.131	0.152(+0)	0.750(+3)
3 0_{-1} 3 0...........	3025.528	516.713	2508.815	2509.075	0.174(+0)	0.863(+3)
2 1_{-1} 2 1...........	2755.291	237.279	2518.012	2518.207	0.837(−1)	0.419(+3)
1 0_{-1} 1 0...........	2616.487	86.933	2529.554	2529.724	0.761(−1)	0.387(+3)
1 1_{+1} 1 1...........	2609.377	64.104	2545.273	2545.418	0.385(−1)	0.199(+3)
2 1_{+1} 2 1...........	2790.127	237.279	2552.849	2552.987	0.216(−1)	0.113(+3)
2 2_{+1} 2 2...........	2723.765	169.246	2554.519	2554.664	0.430(−1)	0.225(+3)
3 3_{+1} 3 3...........	2876.591	315.248	2561.343	2561.493	0.454(−1)	0.239(+3)
3 2_{+1} 3 2...........	2992.161	427.881	2564.279	2564.408	0.324(−1)	0.171(+3)
4 4_{+1} 4 4...........	3069.003	501.875	2567.129	2567.285	0.470(−1)	0.250(+3)
3 1_{+1} 3 1...........	3063.193	494.606	2568.587	N.O.	0.851(−2)	0.452(+2)
5 5_{+1} 5 5...........	3299.725	728.777	2570.947	2571.111	0.481(−1)	0.257(+3)
4 3_{+1} 4 3...........	3233.027	658.503	2574.524	2574.660	0.385(−1)	0.206(+3)
5 4_{+1} 5 4...........	3509.703	928.672	2581.031	2581.184	0.410(−1)	0.221(+3)
4 2_{+1} 4 2...........	3531.023	768.225	2582.798	N.O.	0.162(−1)	0.877(+2)
4 1_{+1} 4 1...........	3422.758	833.311	2589.446	N.O.	0.378(−2)	0.206(+2)
5 3_{+1} 5 3...........	3673.497	1080.139	2593.358	2593.460	0.197(−1)	0.108(+3)
5 2_{+1} 5 2...........	3792.568	1186.725	2605.843	N.O.	0.845(−2)	0.469(+2)
5 1_{+1} 5 1...........	3862.944	1249.910	2613.034	N.O.	0.192(−2)	0.108(+2)
2 1_{-1} 1 1...........	2755.291	64.104	2691.187	2691.444	0.422(−1)	0.258(+3)
2 0_{-1} 1 0...........	2812.642	86.933	2725.709	2725.898	0.777(−1)	0.494(+3)
2 1_{+1} 1 1...........	2790.127	64.104	2726.023	2726.219	0.475(−1)	0.302(+3)
3 2_{-1} 2 2...........	2930.998	169.246	2761.752	2762.068	0.888(−1)	0.587(+3)
3 1_{-1} 2 1...........	3002.486	237.279	2765.207	2765.457	0.222(−1)	0.147(+3)
3 2_{+1} 2 2...........	2992.161	169.246	2822.915	2823.136	0.473(−1)	0.334(+3)
3 1_{+1} 2 1...........	3063.193	237.279	2825.914	2826.113	0.909(−1)	0.643(+3)
4 3_{-1} 3 3...........	3144.790	315.248	2829.542	2829.923	0.135(+0)	0.956(+3)
4 1_{-1} 3 1...........	3325.518	494.606	2830.912	2831.340	0.135(−1)	0.959(+2)

TABLE 2—*Continued*

$J'G'_U$–$J''K''$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	ω_{if}(exp)[b] (cm^{-1})	$S(f-i)$ ($debye^2$)	A_{if} s^{-1}
$4\,2_{-1}$ $3\,2$	3259.663	427.881	2831.782	2832.197	0.566(−1)	0.403(+3)
$5\,1_{-1}$ $4\,1$	3721.811	833.311	2888.500	N.O.	0.921(−2)	0.696(+2)
$5\,2_{-1}$ $4\,2$	3659.563	768.225	2891.338	2891.867	0.385(−1)	0.292(+3)
$5\,4_{-1}$ $4\,4$	3395.911	501.875	2894.037	2894.488	0.178(+0)	0.135(+4)
$5\,3_{-1}$ $4\,3$	3552.620	658.503	2894.117	2894.610	0.910(−1)	0.692(+3)
$4\,3_{+1}$ $3\,3$	3233.027	315.248	2917.779	2918.026	0.497(−1)	0.387(+3)
$4\,1_{+1}$ $3\,1$	3422.758	494.606	2928.152	2928.351	0.126(+0)	0.996(+3)
$4\,2_{+1}$ $3\,2$	3351.023	427.881	2923.142	2923.361	0.100(+0)	0.784(+3)
$4\,0_{-1}$ $3\,0$	3446.685	516.713	2929.972	2930.163	0.134(+0)	0.106(+4)
$5\,4_{+1}$ $4\,4$	3509.703	501.875	3007.828	3008.115	0.552(−1)	0.471(+3)
$5\,3_{+1}$ $4\,3$	3673.497	658.503	3014.994	3015.240	0.113(+0)	0.969(+3)
$5\,2_{+1}$ $4\,2$	3792.568	768.225	3024.343	3024.550	0.142(+0)	0.124(+4)
$5\,1_{+1}$ $4\,1$	3862.944	833.311	3029.633	3029.822	0.160(+0)	0.139(+4)

[a] Powers of 10 in brackets.

[b] Majewski *et al.* 1987.

[c] N.O. denotes transitions not experimentally observed.

motions from its D_{3h} equilibrium symmetry even in low-lying states.

In order to obtain highly accurate results, basis sets 60% larger than previously employed (Miller and Tennyson 1987) were used for both of the variational steps. This meant that energy levels throughout the range considered were converged to better than 0.01 cm^{-1} and line strengths to at least three significant figures. All calculations were carried out using the Cray XMP-48 computer at the Atlas Center at the Rutherford Appleton Laboratories.

III. RESULTS AND DISCUSSION

Selection rules for the "forbidden" rotational spectrum and ν_2 rovibrational transitions are determined by symmetry considerations and nuclear spin statistics. For the pure rotational spectrum this means $\Delta J = 0$ or ± 1 and $\Delta K = 3$. (Transitions from $K = 1$ to $K = 2$ and vice versa are allowed since they are considered to be from -1 to 2 or from -2 to 1.) For the ν_2 transitions, once more $\Delta J = 0$ or ± 1 and only $K = G$ transitions are dipole allowed. In this, and in Tables 1 and 2 we use the notation of Watson *et al.* (1984).

Transition dipole moments, line strengths and Einstein A coefficients for spontaneous emission are given in Table 1 for the forbidden rotational spectrum of H_3^+ in the vibrational ground state. For states with angular momentum up to $J = 8$ it is clear that there are a large number of possible transitions with frequencies ranging from 7 to over 1300 cm^{-1} and transition dipole moments from 2 millidebye to over 0.1 debye. Results previously computed by Jensen and Spirko (1986) are in broad agreement with our calculated line strengths, although their transition frequencies are not so accurate.

Our results differ from those of Pan and Oka in both frequency and line strength. The differences in transition frequencies are due to the factors mentioned above. In general, our line strengths are systematically smaller than those predicted by equation 1 of Pan and Oka. For instance, the $J' = 8$, $K' = 1 - J'' = 8$, $K'' = 2$ line at 56.525 cm^{-1} is predicted to have a line strength of 1.79×10^{-2} D^2 by us, and 2.50×10^{-2} D^2 in their work, a difference of 40%.

There are instances, however, where we calculate line strengths up to 50 per cent greater than Pan and Oka, such as the 7, 0–7, 3 line at 178.247 cm^{-1}, for which we calculate a line strength of 1.79×10^{-2} D^2 and for which Pan and Oka predict a value of 1.18×10^{-2} D^2.

In Table 2 we compare the calculated frequencies for ν_2 rovibrational transitions with those obtained experimentally. The agreement is very close, especially at the lower frequency end of the range considered where the difference between the two values does not exceed 0.1 cm^{-1}. For states with $J \leq 5$, the largest divergence we find is less than 0.5 cm^{-1}. For the 60 lines for which comparison with experiment is possible, we found a root means square deviation of 0.24 cm^{-1}.

Direct comparison between theory and experiment for the line strengths is not possible. We note, however, that, with the exception of the line at 2467.24 cm^{-1}, all transitions calculated to have a line strength of more than 2.0×10^{-2} D^2 are also experimentally observed, while none of those predicted to be weaker than this are seen. We calculate the 5, 0_{-1}–5, 0 at 2471.48 cm^{-1} to have the greatest line strength, $S(f-i) = 0.264$ D^2, for those states with $J \leq 5$.

The selection rules discussed above lead to three or less possible decay routes for the levels presented, and radiative lifetimes may be computed from the Einstein A coefficients via:

$$\tau_f = (\Sigma_i A_{if})^{-1} . \tag{1}$$

where we have defined:

$$A_{if} = \frac{64\pi^4\omega_{if}^3}{3h} S(f-i)$$

$$= \frac{64\pi^4\omega_{if}^3}{3h} M_{if}^2 \tag{2}$$

IV. CONCLUSIONS

Our recalculation of the data for the "forbidden" pure rotational transitions in the ground state of H_3^+ shows differences in frequency and line strength from results derived from perturbation theory. In general, our method computes vibrational ground state energy levels more accurately than those in ν_2. We would therefore expect that our pure rotational transition frequencies are at least as accurate as those for the rovibrational transitions, and probably better.

There is also indirect experimental evidence that the pure rotational transition frequencies we calculate should be very accurate. Two submillimeter line have been measured for the deuterated isotopomer H_2D^+ (Warner *et al.* 1984; Bogey, Demuynck, and Destombes 1984; Saito, Kawaguchi and Hirota 1984). For the 1_{10}–1_{11} transition Warner *et al.* (1984) and Bogey *et al.* (1984) both obtained a figure of 12.414 cm^{-1}. For the 2_{20}–2_{21} line, Saito *et al.* (1984) measured the frequency to be 5.200 cm^{-1}. For these two transitions, we have calculated frequencies of 12.412 cm^{-1} and 5.193 cm^{-1}, respectively (Miller, Tennyson, and Sutcliffe 1988) using the MBB potential energy surface, in very good agreement with experiment.

Dependent on the appropriate astrophysical conditions, a search for the "forbidden" rotational lines of H_3^+ using the line strengths and frequencies given in Table 1 could therefore prove worthwhile.

For his 1981 search, Oka considered the ortho–H_3^+ 2, 0_{-1}–1, 0 and para–H_3^+ 2, 1_{+1}–1, 1 lines at 2725.898 cm^{-1} and 2726.219 cm^{-1} respectively to be promising candidates for observation. For these lines we calculate values of $S(f-i)$ to be 7.77×10^{-2} D^2 and 4.75×10^{-2} D^2, and radiative lifetimes of 1.45 ms and 1.57 ms respectively.

In this paper, we have presented results for those rovibrational transitions which would appear to be most astrophysically useful. Line strengths and frequencies for other transitions—including "hot bands" and isotopically substituted species such as H_2D^+—are available, if required, from the authors on request.

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