1986ApJ...305..518P

THE ASTROPHYSICAL JOURNAL, 305:518–525, 1986 June 1
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CALCULATED FORBIDDEN ROTATIONAL SPECTRA OF H_3^+

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Received 1985 September 17; accepted 1985 November 26

ABSTRACT

The forbidden rotational spectra of the H_3^+ molecular ion have been calculated in the ground state and in the v_2 state, anticipating the observation of such spectra in space and in the laboratory. The small moments of inertia and the large vibrational amplitude of H_3^+ make the former spectrum unusually strong. The Watson coefficient θ_x^{xx} for the centrifugal distortion induced dipole moment and the Mizushima-Venkateswarlu dipole moment have been calculated to be 1.1×10^{-3} and 5.2×10^{-3} debye, respectively. The former is larger by a factor of ~ 50 than that of CH_4, for which the forbidden rotational spectrum has been observed in the laboratory.

The calculated spectral pattern for laboratory observations is given, and the intensities of spontaneous emissions from dense molecular clouds are also discussed.

Subject headings: interstellar: molecules — molecular process

I. INTRODUCTION

The H_3^+ molecular ion, in which three protons are held together by two electrons in an equilateral triangle configuration, is the simplest stable polyatomic system. It is produced abundantly in dense molecular clouds through cosmic-ray ionization of H_2 and the subsequent efficient ion-molecule reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H \, .$$

A detailed chemical equilibrium calculation in dense clouds by de Jong, Dalgarno, and Boland (1983) predicts a column density of H_3^+ which is on the order of 10^{14} cm^{-2}, comparable to that of HCO^+, the spectrum of which has been observed very strongly by radio astronomers. The H_3^+ molecular ion plays a crucial role in the ion-molecule reaction scheme for producing interstellar molecules (Herbst and Klemperer 1973; Watson 1976; Suzuki 1979). The spectroscopic detection of interstellar H_3^+ is therefore highly desirable, not only because it provides astronomers with a third hydrogenic species (after H and H_2) for probing interstellar conditions, but also because it provides probes for the basic chemical conditions in dense clouds.

The recent laboratory discovery of the infrared spectrum of H_3^+ (Oka 1980) gives the first vehicle for such an attempt, and a few (negative or inconclusive) results have been reported (Oka 1981; Burton, von Nagy-Felsobuki, and Smith 1983). One intrinsic difficulty in attempting the infrared observation of H_3^+ in absorption is the requirement that a relatively intense infrared source has to exist behind the dense molecular cloud, a requirement which limits the possible observation region to few special sources (Oka 1981).

In this paper we point out an alternative possibility of detecting interstellar H_3^+, i.e., the possibility of detecting it through its forbidden rotational spectrum. The possibility of detecting the monodeuterated H_2D^+ species through its microwave spectrum have already been pointed out (Dalgarno *et al.* 1973), and a possible detection of such a spectral line has recently been reported (Phillips *et al.* 1985). While H_3^+ does not possess a permanent electric dipole moment in its equilibrium configuration because of the equilateral triangle structure, a small dipole moment induced by distortion of the equilibrium geometry through rotation or vibration produces a forbidden rotational spectrum. Normally such spectral lines are extremely weak, and special techniques are employed to observe them in the laboratory (see Oka 1976 for a review). In H_3^+, however, the small moments of inertia, the large vibrational amplitude, and the large dipole derivatives make the forbidden spectra stronger by orders of magnitude than those of normal molecules such as NH_3 and CH_4. Astronomical applications of forbidden rotational transitions were earlier discussed for the thermal equilibration of interstellar NH_3 (Oka *et al.* 1971) and for the detection of interstellar CH_4 (Barrett 1978). The reported observation of CH_4 transitions (Fox and Jennings 1978) remains controversial (Ellder *et al.* 1980; Ozier, Gerry, and Robiette 1981; Wilson and Synder 1985). The rotational spectrum of H_3^+ has also been recently discussed by Aliev and Mikhailov (1984), but their results are considerably different from ours because of the different values of dipole moment functions used.

II. $\Delta k = \pm 3$ ROTATIONAL TRANSITIONS IN THE GROUND STATE

If a nonpolar molecule does not possess a center of symmetry, as in H_3^+, the centrifugal distortion perpendicular to the C_3 axis breaks the C_3 symmetry of the molecule and produces a small dipole moment in the plane of the molecule, which induces pure rotational transitions in which the signed rotational quantum number k (the projection of the total angular momentum along the molecular axis) changes by a unit of 3. The general theory for such transitions has been worked out by Watson (1971). The theory gives the line strengths of the forbidden transitions as

$$S[(J', k') \leftarrow (J, k)] = \sum_{f, m', m} |\langle J', k', m' | \mu_f | J, k, m \rangle|^2$$
$$= \tfrac{1}{4}(\theta_x^{xx})^2 F[(J', k') \leftarrow (J, k)] \, , \qquad (1)$$

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where $F[(J', k') \leftarrow (J, k)]$ are

$$(J \mp k)(J \mp k - 1)(J \pm k + 1)(J \pm k + 2)(J \pm k + 3) \times (J \pm k + 4)/(J + 1)$$

for $(J + 1, k \pm 3) \leftarrow (J, k)$;

$$(J \mp k)(J \mp k - 1)(J \mp k - 2)(J \pm k + 1)(J \pm k + 2) \times (J \pm k + 3)(2J + 1)/J(J + 1)$$

for $(J, k \pm 3) \leftarrow (J, k)$; and

$$(J \mp k)(J \mp k - 1)(J \mp k - 2)(J \mp k - 3)(J \pm k + 1) \times (J \pm k + 2)/J$$

for $(J - 1, k \pm 3) \leftarrow (J, k)$, respectively.

The Watson coefficient for the distortion-induced dipole moment θ_x^{xx} is simplified for H_3^+ as

$$\theta_x^{xx} = 2\left(\frac{B}{\nu_2}\right)^{3/2} \frac{\partial \mu}{\partial q_2}, \tag{2}$$

where B and ν_2 are the rotational constant ($B = 43.6$ cm^{-1}) and the vibrational frequency of the degenerate ν_2 mode ($\nu_2 = 2521.3$ cm^{-1}), respectively, and $\partial\mu/\partial q_2$ is the dipole derivative with respect to the dimensionless ν_2 normal coordinate. Equation (2) can be derived by substituting $\partial I_{xx}/\partial Q_2 \equiv a_{2x}^{(xx)} = (2I_{xx})^{1/2}$ and $Q_2 = (1/2\pi)(h/c\nu_2)^{1/2} q_2$ into Watson's general formula. The former relation between the derivative of the moment of inertia (along the in-plane axis x) I_{xx} with respect to the normal coordinate Q_2 and the moment of inertia I_{xx} can be obtained either from a direct calculation of the normal coordinate or from the general relation (Oka 1967) for a molecule with C_3 axis of symmetry for which

$$-a_{tx}^{(xx)} = a_{tx}^{(yy)} = a_{ty}^{(xy)}, \quad \text{and} \sum_t [a_{ty}^{(xy)}]^2 = I_{zz}.$$

For H_3^+, the moment of inertia along the out-of-plane axis z is $I_{zz} = 2I_{xx}$. The second term for $(\theta_x^{xx})_{\text{eff}}$ in Watson's formula (1971) is zero for H_3^+ because of its planar symmetry.

The numerical values used in the calculation of frequencies and intensities of the spectrum are listed in Table 1. The rotational constants were taken from Watson *et al.* (1984). The values of dipole derivatives given in the extensive ab initio calculation of H_3^+ by Carney and Porter (1974) were used after transforming them to a suitable unit. For example, $\partial\mu/\partial S_2 = 0.428$ a.u. was translated to $\partial\mu/\partial q_2 = 0.238$ debye. The calculated value of

$$\theta_x^{xx} = 1.08 \times 10^{-3} \text{ debye}$$

is greater than the corresponding values of NH_3 (Oka *et al.* 1971) and CH_4 (Ozier 1971) by 8 and 50, respectively. Thus the line strength of H_3^+ is larger by orders of magnitude than that of CH_4 which have been observed in the laboratory (Rosenberg, Ozier, and Kudian 1972; Curl, Oka, and Smith 1973; Holt, Gerry, and Ozier 1973).

The rotational energy levels of H_3^+ in the ground state and the forbidden rotational transitions are shown in Figure 1. The rotational wave functions have to be antisymmetric with respect to the (12) proton permutation, and thus only wave functions

$$[|J, k\rangle - (-1)^J |J, -k\rangle] \quad \text{for } k \neq 0,$$

and

$$|J, 0\rangle \quad \text{with } J \text{ odd}$$

are allowed. This results from the relation (Hougen 1962)

$$(12)|J, k\rangle = (-1)^J |J, -k\rangle.$$

The parity of the wave function is given by $(-1)^K$ and is shown in the figure. The levels with $k = 3n$ correspond to ortho-H_3^+ ($I = 3/2$), and those with $k = 3n \pm 1$ to para-H_3^+ ($I = 1/2$); they do not convert from one to the other easily [because of the (123) permutation symmetry]. Since the lowest rotational level $J = K = 0$ is not allowed as shown above, the $J = K = 1$ level is the ground rotational level. The level $J = 1$, $K = 0$, which is 23.2 cm^{-1} above the lowest level, is also very stable because the ortho-para conversion is highly forbidden. Thus, at low temperature of dense molecular clouds, H_3^+ exists mostly in these two lowest levels. The proton exchange reaction

TABLE 1

MOLECULAR CONSTANTS OF H_3^+ USED FOR THE CALCULATION OF FREQUENCIES AND INTENSITIES OF FORBIDDEN ROTATIONAL TRANSITIONS

Parameter	Value
Ground-State Rotational Constants[a]	
B	43.564570
C	20.605147
D_J	4.17537×10^{-2}
D_{JK}	-7.60626×10^{-2}
D_K	3.74107×10^{-2}
h_3	-1.056×10^{-5}
d_J	1.7325×10^{-3}
d_K	-4.1003×10^{-3}
Excited State Constants[a]	
ν_2	2521.30817
q_2	−5.37192
ϕ_{222}	−1183
Dipole Moment Derivatives	
$\left(\frac{\partial\mu}{\partial S_2}\right)$	0.428 a.u.[b]
$\left(\frac{\partial^2\mu}{\partial S_2^2}\right)$	−0.878 a.u.[b]
$\left(\frac{\partial\mu}{\partial q_2}\right)$	0.237 debye
$\left(\frac{\partial^2\mu}{\partial q_2^2}\right)$	−0.106 debye
Transition Moments	
θ_x^{xx}	$2\left(\frac{B}{\nu_2}\right)^{3/2}\left(\frac{\partial\mu}{\partial q_2}\right) = 1.08 \times 10^{-3}$ debye
μ_v	$\left(\frac{\partial^2\mu}{\partial q_2^2}\right) + \frac{\phi_{222}}{\nu_2}\left(\frac{\partial\mu}{\partial q_2}\right) = -5.20 \times 10^{-3}$ debye

[a] In cm^{-1}. From Watson *et al.* 1985.
[b] Carney and Porter 1974.

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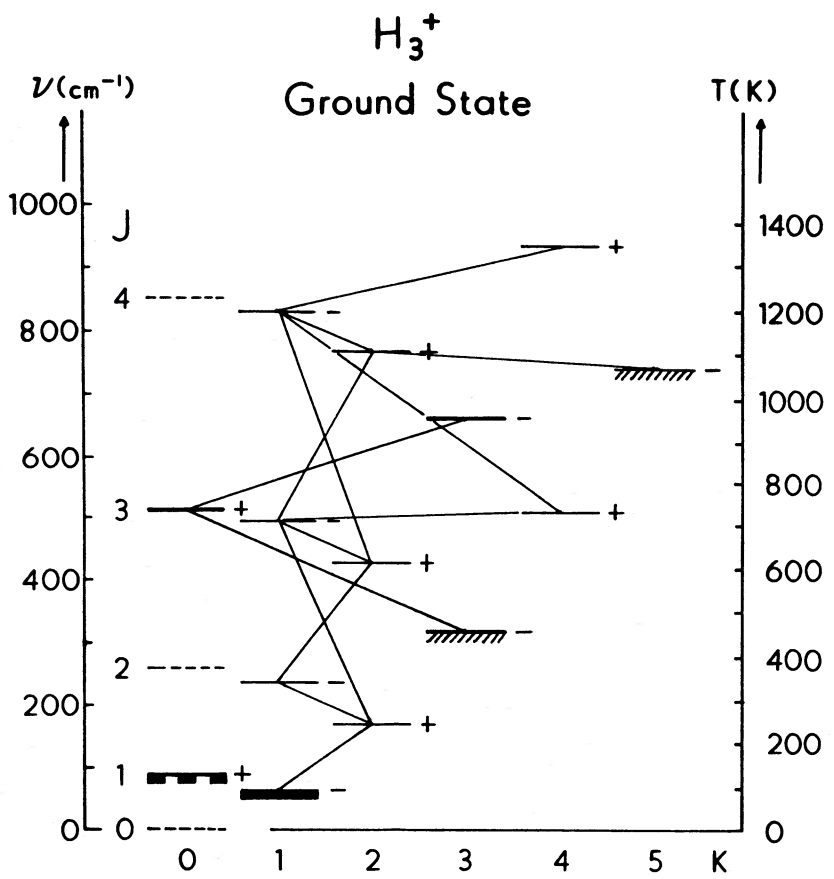


FIG. 1.—Rotational energy levels of H_3^+ in the ground vibrational state. Three types of "stable" levels are indicated; the lowest ($J = 1$, $K = 1$) level by a bold line, the ($J = 1$, $K = 0$) level which is metastable both collisionally and radiatively by a broken bold line, and the ($J = 5$, $K = 5$) and ($J = 3$, $K = 3$) levels which are metastable for radiative transitions by shadowed lines. The forbidden rotational transitions are shown by lines connecting levels.

(Dalgarno, Black, and Weisheit 1973) will equilibrate these two states.

The selection rules for the forbidden rotational transitions (which are shown with arrows) are

$$\Delta J = 0, \pm 1 \quad \text{and} \quad \Delta k = \pm 3 .$$

The $K = 2 \leftrightarrow 1$ transitions in Figure 1 are understood to be $k = \pm 2 \leftrightarrow \mp 1$. Note also the parity rule " $+ \leftrightarrow -$ " is automatically satisfied by the k rule.

The vibration-rotation parameters of H_3^+ recently obtained by Watson *et al.* (1984) were used to calculate the rotational spectrum. The calculated frequencies, the effective transition dipole moment μ_{ij}, the Einstein probability for spontaneous emission for interstellar H_3^+, and the absorption cross section are listed in Table 2. The uncertainties of the calculated frequencies are ~ 0.05 cm^{-1}. The largest source of error for the calculated frequencies is the uncertainty of the C_0 rotational constant which is not directly determined from the experimental results (Watson *et al.* 1984). The spontaneous emission rate was calculated from

$$A = \frac{4\omega^3}{3\hbar c^3} |\mu_{ij}|^2 , \tag{3}$$

and the absorption cross section from

$$\sigma = \frac{4\pi}{3\hbar c} f_r f_v \left[1 - \exp\left(- \frac{h\nu}{kT} \right) \right] |\mu_{ij}|^2 \frac{\nu}{\Delta\nu} , \tag{4}$$

where $f_r f_v$ is the fraction of H_3^+ in the rotational level of interest, and $\Delta\nu = \nu/c(2kT/m)^{1/2}$ is the Doppler width of the spectral line. The absorption coefficient in the laboratory can be obtained by multuplying by the ion number density (typically 10^{11} cm^{-3}) to the calculated cross section. The rotational and translational temperatures were assumed to be equal, and the calculation was made for the typical plasma conditions of 200 K (liquid N_2 cooled), 500 K (water cooled), and 1000 K (air cooled). The overall picture of the H_3^+ rotational spectrum is shown in Figure 2.

It may be noted from Table 2 and Figure 2 that H_3^+ has a rich rotational spectrum in the range of millimeter-wave to mid-infrared region. The spontaneous emission is much faster than the corresponding case of NH_3 forbidden transition (Oka *et al.* 1969), and most H_3^+ ions reach their lowest rotational level within a few weeks (compared to 100 yr of NH_3). It is noted in Figure 1 that H_3^+ in the levels with $J = K = 5, 5$ and 3, 3 are metastable in the sense that spontaneous emission does not transfer them to lower levels; collision, which also obeys $K = \pm 3$ rules (Oka 1968), transfers them to lower levels. The

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TABLE 2

CALCULATED FREQUENCIES, TRANSITION DIPOLE MOMENTS, EINSTEIN COEFFICIENTS FOR SPONTANEOUS EMISSION, AND ABSORPTION CROSS SECTIONS FOR ROTATIONAL TRANSITIONS OF H_3^+ OF THE GROUND STATE[a]

TRANSITIONS $(J, K)_u$–$(J, K)_L$	FREQUENCIES (cm^{-1})	$\lvert\mu_{ij}\rvert$ (mD)	A_{ij} (s^{-1})	ABSORPTION CROSS SECTIONS (10^{-16} cm^2) T = 200 K	T = 500 K	T = 1000 K
4 4 3 1.....	7.178	5.9	4.1(−9)	2.3(−5)	1.3(−5)	3.1(−6)
7 6 6 3.....	8.162	18	5.6(−8)	3.7(−7)	2.2(−5)	2.6(−5)
7 4 8 7.....	31.520	21	4.1(−6)	6.5(−8)	2.2(−5)	4.6(−5)
4 2 5 5.....	39.609	7.3	1.0(−6)	5.0(−5)	8.2(−5)	2.8(−5)
6 5 5 2.....	50.983	14	5.7(−6)	8.9(−6)	1.1(−4)	7.4(−5)
8 1 8 2.....	56.651	38	8.4(−5)	5.9(−10)	1.0(−5)	7.8(−5)
7 1 7 2.....	58.892	30	5.7(−5)	2.9(−8)	3.4(−5)	1.1(−4)
6 1 6 2.....	61.105	22	3.5(−5)	8.3(−7)	8.6(−5)	1.2(−4)
5 1 5 2.....	63.210	16	1.9(−5)	1.2(−5)	1.5(−4)	1.1(−4)
4 1 4 2.....	65.126	10	9.1(−6)	9.1(−5)	1.9(−4)	7.0(−5)
3 1 3 2.....	66.773	5.9	3.3(−6)	2.8(−4)	1.3(−4)	3.0(−5)
2 1 2 2.....	68.079	2.6	6.9(−7)	2.6(−4)	4.0(−5)	6.4(−6)
5 3 6 6.....	84.851	9.4	1.7(−5)	5.3(−5)	3.0(−4)	1.6(−4)
5 4 4 1.....	95.228	11	3.2(−5)	8.4(−5)	2.4(−4)	1.0(−4)
8 6 7 3.....	99.569	26	2.2(−4)	1.4(−7)	1.2(−4)	3.2(−4)
2 2 1 1.....	105.154	1.5	8.5(−7)	1.5(−4)	1.6(−5)	2.2(−6)
6 4 7 7.....	129.312	12	9.1(−5)	6.7(−6)	1.5(−4)	1.3(−4)
7 5 6 2.....	137.852	21	3.8(−4)	1.4(−6)	1.6(−4)	2.4(−4)
4 3 3 0.....	141.771	7.2	4.7(−5)	7.4(−4)	5.8(−4)	1.6(−4)
7 5 8 8.....	172.539	14	3.0(−4)	1.1(−6)	1.2(−4)	1.6(−4)
7 0 7 3.....	179.083	28	1.4(−3)	2.3(−7)	2.1(−4)	6.1(−4)
6 4 5 1.....	180.215	16	4.9(−4)	1.7(−5)	3.4(−4)	2.8(−4)
3 2 2 1.....	190.639	3.7	3.0(−5)	6.1(−4)	1.6(−4)	3.0(−5)
5 0 5 3.....	190.900	14	4.3(−4)	8.8(−5)	8.5(−4)	5.4(−4)
3 0 3 3.....	201.594	4.2	4.5(−5)	1.3(−3)	4.6(−4)	9.8(−5)
8 5 7 2.....	220.161	29	2.8(−3)	6.4(−8)	9.7(−5)	3.4(−4)
7 4 6 1.....	261.319	23	2.8(−3)	1.3(−6)	2.4(−4)	4.2(−4)
4 2 3 1.....	273.677	6.7	2.9(−4)	5.0(−4)	4.3(−4)	1.3(−4)
8 1 8 4.....	286.772	34	8.3(−3)	6.1(−9)	5.7(−5)	3.6(−4)
7 1 7 4.....	298.608	25	5.2(−3)	2.9(−7)	1.8(−4)	4.5(−4)
6 3 5 0.....	306.228	16	2.4(−3)	3.6(−5)	9.3(−4)	8.4(−4)
6 1 6 4.....	310.313	17	2.8(−3)	7.6(−6)	3.9(−4)	4.5(−4)
5 1 5 4.....	321.464	11	1.2(−3)	9.4(−5)	5.7(−4)	3.1(−4)
3 1 2 2.....	325.491	2.4	6.1(−5)	4.8(−4)	1.1(−4)	2.0(−5)
4 1 4 4.....	331.625	5.4	3.4(−4)	4.2(−4)	4.0(−4)	1.2(−4)
8 4 7 1.....	337.909	29	1.0(−2)	5.0(−8)	1.1(−4)	4.5(−4)
5 2 4 1.....	353.482	10	1.5(−3)	1.4(−4)	6.0(−4)	2.9(−4)
4 1 3 2.....	405.575	5.0	5.2(−4)	4.9(−4)	3.7(−4)	1.0(−4)
8 2 8 5.....	406.761	29	1.8(−2)	1.8(−8)	8.6(−5)	4.5(−4)
7 2 7 5.....	424.288	20	9.9(−3)	8.0(−7)	2.5(−4)	5.1(−4)
6 2 5 1.....	429.423	15	5.5(−3)	1.9(−5)	5.0(−4)	4.6(−4)
6 2 6 5.....	441.650	13	4.5(−3)	1.8(−5)	4.6(−4)	4.2(−4)
8 3 7 0.....	456.820	28	2.4(−2)	8.5(−8)	2.3(−4)	1.0(−3)
5 2 5 5.....	458.218	6.5	1.3(−3)	1.5(−4)	4.4(−4)	1.9(−4)
5 1 4 2.....	481.818	8.4	2.5(−3)	1.6(−4)	5.4(−4)	2.6(−4)
7 2 6 1.....	501.034	20	1.6(−2)	1.2(−6)	2.8(−4)	5.5(−4)
8 3 8 6.....	536.334	23	2.6(−2)	1.1(−7)	2.4(−4)	9.6(−4)
6 1 5 2.....	553.738	12	8.3(−3)	2.1(−5)	4.7(−4)	4.2(−4)
7 3 7 6.....	555.568	15	1.2(−2)	4.5(−6)	5.6(−4)	9.0(−4)
8 2 7 1.....	568.030	26	3.9(−2)	4.2(−8)	1.2(−4)	5.2(−4)
6 3 6 6.....	581.978	7.4	3.4(−3)	7.0(−5)	7.0(−4)	4.8(−4)
5 0 4 3.....	612.560	5.7	2.4(−3)	3.3(−4)	7.7(−4)	3.3(−4)
7 1 6 2.....	621.032	17	2.3(−2)	1.4(−6)	2.7(−4)	5.1(−4)
8 4 8 7.....	668.037	16	2.5(−2)	2.0(−7)	1.4(−4)	4.1(−4)
8 1 7 2.....	683.573	23	5.3(−2)	5.0(−8)	1.1(−4)	4.9(−4)
7 4 7 7.....	700.944	8.3	7.4(−3)	5.6(−6)	2.2(−4)	2.5(−4)
7 0 6 3.....	742.813	14	2.5(−2)	3.8(−6)	5.0(−4)	8.5(−4)
5 1 4 4.....	748.318	3.0	1.1(−3)	1.4(−4)	1.7(−4)	6.2(−5)
6 1 5 4.....	811.992	6.2	6.4(−3)	3.4(−5)	2.8(−4)	1.9(−4)
8 5 8 8.....	816.988	9.0	1.4(−2)	6.5(−7)	1.2(−4)	2.2(−4)
7 1 6 4.....	870.240	10	2.1(−2)	2.9(−6)	2.1(−4)	3.1(−4)
8 1 7 4.....	923.289	15	5.5(−2)	1.2(−7)	1.0(−4)	3.5(−4)
6 2 5 5.....	950.850	3.1	2.6(−3)	3.6(−5)	1.3(−4)	6.8(−5)
7 2 6 5.....	1003.790	6.5	1.3(−2)	4.8(−6)	1.5(−4)	1.8(−4)
8 2 7 5.....	1051.210	11	4.2(−2)	2.3(−7)	9.3(−5)	2.5(−4)
7 3 6 6.....	1145.709	3.2	4.8(−3)	1.3(−5)	1.5(−4)	1.3(−4)
8 3 7 6.....	1191.471	6.7	2.4(−2)	9.8(−7)	1.4(−4)	2.8(−4)
8 4 7 7.....	1337.461	3.3	8.0(−3)	8.8(−7)	3.9(−5)	5.2(−5)

[a] Numbers in parentheses show powers of 10.

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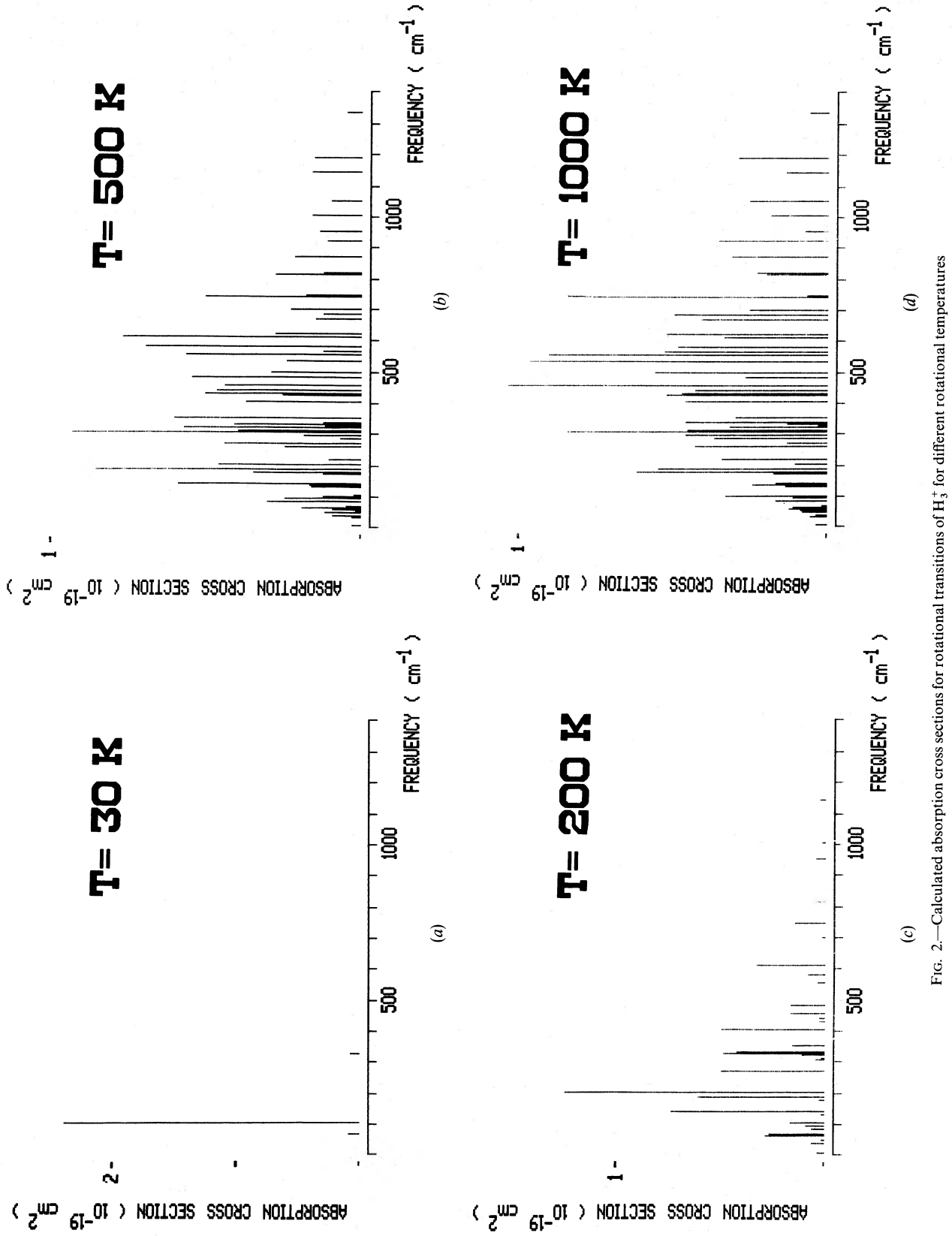


FIG. 2.—Calculated absorption cross sections for rotational transitions of H_3^+ for different rotational temperatures

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calculated absorption cross section of $\sim 10^{-19}$ cm^2 suggests that the laboratory observation of the rotational spectrum is difficult but not out of the question, especially in view of the improved technique of higher production of H_3^+ in hollow cathode discharge and higher sensitivity of laser spectroscopy (Watson *et al.* 1984). The transition moment for $J \approx 10$ is comparable to the infrared transition moment of 0.158 debye.

III. $\Delta|k-l| = 3$ ROTATIONAL TRANSITIONS IN THE v_2-STATE

For H_3^+ in the degenerate v_2 state, the cubic vibrational anharmonicity breaks down the geometrical symmetry of the molecule and produces a small vibration-induced dipole moment, as initially predicted by Mizushima and Venkateswarlu (1953). According to the subsequent more general formulation of Mills, Watson, and Smith (1969), the dipole moment is given by

$$\mu_v = \frac{\partial^2 \mu}{\partial q_2^2} - \frac{\phi_{222}}{v_2}\frac{\partial \mu}{\partial q_2}, \tag{5}$$

where ϕ_{222} is the cubic anharmonicity constant in units of cm^{-1}. Equation (5) is obtained by replacing normal coordinate Q with the dimensionless normal coordinate q in the formula of Mills, Watson, and Smith (1969). The value of ϕ_{222} is calculated to be -1183 cm^{-1} from the observed l-doubling constant $q = -5.37$ cm^{-1} (Watson *et al.* 1984) and from the formula

$$q = 2\left(\frac{B}{v}\right)^{3/2}\phi_{222}, \tag{6}$$

which is obtained from the general formula of l-doubling constant (Grenier-Besson 1964) by noting that all off-diagonal Coriolis constants are zero and that $\phi_{222} = 3!k_{222}$. The values of q and ϕ_{222} are extraordinarily large for H_3^+ even compared with the "giant" l-doubling of NH_3 (Garing, Nielson, and Rao 1959). The value of $\partial\mu/\partial q_2$ has already been given in the last section. The value of the second derivative $\partial^2\mu/\partial q_2^2$ is obtained from the calculation of Carney and Porter (1974) to be 0.106 debye. One complication occurs in relation to the relative sign of the two terms in equation (5). This information is provided by the Carney and Porter calculation for the spontaneous emission rate for the overtone band $2v_2 \rightarrow 0$. The transition dipole moment for such a transition is given by Mills, Watson, and Smith (1969) to be

$$\mu_{2\rightarrow 0} = \frac{1}{\sqrt{2}}\left[\frac{\partial^2\mu}{\partial q_2^2} + \frac{\phi_{222}}{3v_2}\frac{\partial\mu}{\partial q_2}\right]. \tag{7}$$

In order for the spontaneous emission time given by Carney and Porter to agree with our calculated value, we had to take the relative sign of the two terms in equation (7) to be equal. This also agrees with the signs of constants given in Table 1. This means that the two terms in equation (5) subtract from each other and make the transition dipole moment for the forbidden rotational lines very small, i.e., 5.2×10^{-3} debye. Thus laboratory detection of such rotational transition will not be easy. The rotational transitions due to vibration-induced dipole moments have earlier been observed by using the highly sensitive double-resonance technique for tetrahedral molecules (Curl and Oka 1973; Takami, Uehara, and Shimoda 1973) and very recently for symmetric top molecules (Yamamato *et al.* 1985).

The calculated frequencies and absorption cross section for the vibration-induced rotational spectrum of H_3^+ are given in Table 3. For the calculation of frequencies, the molecular constants reported by Watson *et al.* (1984) and the observed

TABLE 3

CALCULATED FREQUENCIES AND ABSORPTION CROSS SECTIONS FOR ROTATIONAL TRANSITIONS OF H_3^+ IN THE v_2 STATE

TRANSITIONS $(J', G', U')_u$–$(J, G, U)_L$	FREQUENCIES (cm^{-1})	ABSORPTION CROSS SECTIONS (10^{-16} cm^2)	
		$T = 200$ K	$T = 500$ K
1 0 −1 2 3 1...	2.466	1.1(−12)	6.9(−9)
4 4 1 3 1 1...	5.639	2.8(−14)	1.2(−9)
3 1 −1 3 2 1...	10.489	5.0(−14)	1.6(−9)
4 2 1 4 1 −1...	25.247	2.7(−14)	3.8(−9)
4 1 1 5 4 −1...	26.687	1.6(−15)	3.0(−10)
1 2 1 0 1 1...	26.734	7.2(−12)	3.1(−8)
2 1 −1 2 2 1...	31.622	4.1(−13)	4.3(−9)
2 1 −1 3 4 1...	36.167	4.7(−12)	4.9(−8)
5 5 1 4 2 −1...	39.545	1.3(−13)	1.4(−8)
4 2 1 5 5 1...	51.605	4.6(−14)	6.0(−9)
1 1 1 1 2 1...	61.394	9.1(−12)	4.8(−8)
5 1 −1 5 2 −1...	61.932	1.8(−15)	1.1(−9)
3 3 1 2 0 1...	63.923	6.2(−12)	1.0(−7)
4 1 −1 4 2 −1...	65.916	1.8(−14)	2.1(−9)
3 1 −1 4 4 1...	66.216	8.6(−13)	3.2(−8)
2 1 1 2 2 1...	66.401	3.8(−12)	4.2(−8)
3 2 −1 4 5 1...	67.490	4.1(−12)	8.4(−8)
5 0 −1 5 3 1...	68.953	1.5(−14)	1.0(−8)
5 4 −1 4 1 −1...	70.323	4.1(−14)	6.2(−9)
5 1 1 5 2 1...	70.400	3.9(−16)	4.5(−10)
5 2 1 5 1 −1...	70.887	4.5(−15)	3.8(−9)
2 1 1 3 4 1...	70.951	1.7(−12)	1.9(−8)
3 1 1 3 2 1...	71.055	5.7(−13)	2.1(−8)
3 1 −1 3 2 −1...	71.557	6.4(−14)	1.8(−9)
4 1 1 4 2 1...	71.763	4.2(−14)	7.2(−9)
5 4 1 4 1 1...	84.940	2.9(−14)	6.9(−9)
4 3 −1 5 6 1...	97.737	3.8(−12)	1.8(−7)
5 3 −1 4 0 1...	106.221	3.1(−14)	8.5(−9)
2 2 1 1 1 1...	114.402	1.8(−11)	1.4(−7)
4 3 −1 3 0 −1...	119.258	2.7(−13)	1.2(−8)
3 2 1 4 5 1...	128.562	9.6(−13)	2.2(−8)
3 1 1 3 2 −1...	132.123	2.0(−13)	6.3(−9)
3 2 −1 2 1 1...	141.001	8.1(−13)	1.4(−8)
3 0 −1 3 3 1...	149.172	6.1(−12)	1.5(−7)
4 1 1 4 2 −1...	162.926	5.2(−14)	7.0(−9)
3 2 −1 2 1 −1...	175.780	2.4(−13)	3.7(−9)
5 4 1 4 1 −1...	183.950	1.4(−13)	2.6(−8)
4 3 1 5 6 1...	185.818	7.2(−13)	4.0(−8)
5 0 −1 5 3 −1...	189.572	2.4(−14)	1.2(−8)
4 2 −1 3 1 1...	196.727	2.9(−13)	1.7(−8)
2 0 1 2 3 1...	198.640	2.7(−11)	2.3(−7)
3 2 1 2 1 1...	202.069	6.5(−12)	1.2(−7)
5 1 1 5 2 −1...	203.067	4.9(−15)	3.9(−9)
4 3 1 3 0 −1...	207.361	2.8(−12)	1.5(−7)
2 1 −1 1 2 1...	207.418	1.1(−12)	7.4(−9)
5 1 −1 5 4 1...	212.417	2.9(−14)	1.2(−8)
4 0 1 4 3 1...	213.727	6.9(−13)	9.0(−8)
5 3 1 4 0 1...	226.851	1.3(−13)	4.4(−8)
3 2 1 2 1 −1...	236.848	1.8(−12)	3.1(−8)
5 2 −1 4 1 1...	237.206	3.4(−14)	1.0(−8)
2 1 1 1 2 1...	242.197	5.8(−12)	4.1(−8)
4 1 −1 4 4 1...	257.000	6.5(−13)	4.4(−8)
4 2 −1 3 1 −1...	257.293	2.4(−13)	1.2(−8)
3 1 −1 2 2 1...	278.959	1.3(−12)	2.1(−8)
3 1 −1 3 4 1...	283.505	5.1(−12)	7.8(−8)
4 2 1 3 1 1...	287.890	8.8(−13)	6.1(−8)

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vibration-rotation spectrum of H_3^+ were used. A complication resulted for the calculation of intensities because of the large l-resonance effect between $(K + 1, l = 1)$ and $(K - 1, l = -1)$ levels in the v_2 state. This effect in general made the transition dipole moment even smaller.

ROTATIONAL SPECTRUM OF H_3^+ IN INTERSTELLAR SPACE

The stabilities of rotational levels of H_3^+ in interstellar space are indicated in Figure 1. The $J = 1$, $K = 1$ level is the lowest of all and is most populated if the temperature is very low ($T < 47.4$ K). The $J = 1$, $K = 0$ (1, 0) level is 22.846 cm^{-1} above the lowest $J = 1$, $K = 1$ (1, 1) level but is very stable because the transition to the lower level is forbidden due to the ortho-para rule both radiatively and collisionally (Oka 1968). The relaxation from the (1, 0) to (1, 1) level occurs through the exchange reaction

$$H_3^+ + \tilde{H}_2 \rightarrow \tilde{H}_2 H^+ + H_2 , \tag{8}$$

which has a large cross section (Adam and Smith 1981). Thus, if the hydrogen number density is high, the (1, 0) level is thermalized with the (1, 1) level. The former has larger molecular population than the latter for $T > 47.4$ K on account of its higher spin statistical weight. Unfortunately, the (1, 0) level is isolated in Figure 1, and no rotational transition is expected to take place from it. The (3, 3) and (5, 5) levels are metastable in that no radiative transitions are allowed from them to lower levels, but they are relaxed by collision to lower levels (such as to (1, 0) or (3, 3).

The above consideration suggests that for a cold, dense, molecular cloud the far-infrared emission (2, 2)→(1, 1) predicted at 105.15 cm^{-1} with a spontaneous emission time of 1.2×10^6 s should be the most prominent spectral line. The excitation to the upper level will be achieved through collision with H_2 molecules, either by rotational excitation or exchange reactions such as that given in equation (8). For this system, the molecular populations, n_1 and n_2, in the two levels are well represented by two-level rate equations

$$[k_{21} + B\rho(\nu)]n_1 = [k_{12} + B\rho(\nu) + A]n_2 , \tag{9}$$

where k_{ij} is the collision rate constants for the process $i \leftarrow j$, A and B are the Einstein coefficients for the spontaneous and induced emission, and $\rho(\nu)$ is the energy density coefficient of radiation in the space under consideration. According to the principle of detailed balancing,

$$\frac{k_{21}}{k_{12}} = \frac{g_2}{g_1} \exp\left[-\frac{h\nu}{kT_k} \right], \tag{10}$$

and

$$\frac{B\rho(\nu)}{A + B\rho(\nu)} = \frac{g_2}{g_1} \exp\left[-\frac{h\nu}{kT_r} \right], \tag{11}$$

where g_1 and g_2 are degeneracies of the levels 1 and 2, $h\nu = E_2 - E_1$, and T_k and T_r are the kinetic and radiative temperatures, respectively. From equations (9) (10), (11) we obtain the intensity of emission

$$\begin{aligned} I &= \frac{h\nu}{4\pi} [An_2 + (n_2 - n_1)B\rho(\nu)] \\ &= \frac{h\nu}{4\pi} \frac{[A + B\rho(\nu)]k_{12} n}{k_{12} + k_{21} + A + 2B\rho(\nu)} \frac{g_2}{g_1} \\ &\quad \times \left[\exp\left(-\frac{h\nu}{kT_k} \right) - \exp\left(-\frac{h\nu}{kT_r} \right) \right], \end{aligned} \tag{12}$$

where $n = n_1 + n_2$ is the total column density of the molecular ions. This equation can also be derived from the standard formula of radiative transfer for a low optical depth ($\tau \ll 1$). For dense clouds $T_k \gg T_r$ and $A \gg B\rho(\nu)$ for 105 cm^{-1}. We therefore obtain an approximate formula

$$I \approx \frac{h\nu}{4\pi} \frac{Ak_{12} n}{k_{12} + k_{21} + A} \frac{g_2}{g_1} \exp\left(-\frac{h\nu}{kT_k} \right). \tag{13}$$

If $k_{12} \gg A$, the intensity is proportional to the spontaneous emission rate A, whereas if $A \gtrsim k_{12}$, P is independent of A. Since $A = 8.5 \times 10^{-7}$ s^{-1} for the transition in question, the latter is the case unless the number density of the collision partner H_2 is much higher than 4×10^3 cm^{-3} (H_2 thermal velocity of 4×10^4 cm s^{-1} and collision cross section of 5×10^{-15} cm^2 are assumed). For such a condition the intensity of the emission signal depends only on the total column density, and forbidden transitions should be equally strong as allowed transitions. An order of magnitude calculation shows that a column density of at least 10^{16}–10^{17} cm^{-2} is required to detect the emission for the current instrumental sensitivity. This is much higher than the required column density of 10^{14} cm^{-2} for detecting infrared absorption (Oka 1981). Such a high column density of H_3^+ may exist for highly depleted clouds, although collision pumping may not be sufficient for such clouds because of low temperature.

We wish to thank G. Blake for a useful discussion on the sensitivity of far-infrared observational spectroscopy. This work was supported by NSF grant PHY 84-08316.

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Note added in proof.—Recently Per Jensen and V. Spirko have submitted a paper on the line strengths of H_3^+ to the *Journal of Molecular Spectroscopy* in which the forbidden rotational transitions are discussed. Their calculated intensities are systematically lower than ours by 20%–40% probably because of a different method of calculation.

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