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Difference frequency laser spectroscopy of the ν_3 band of the CH_3 radical

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The ν_3 fundamental band of the CH_3 radical has been detected in absorption with a tunable difference frequency laser. Zeeman modulation is found to be inefficient, because the spin-rotation interaction is small. The molecular constants in the ν_3 vibrational state have been determined with the molecular constants in the ground state fixed at the values determined from the analysis of the ν_2 band. The main parameters thus obtained are the band origin $\nu_0 = 3160.8212(12)$, $B_3 = 9.471\,10(14)$, $C_3 = 4.701\,67(15)$, $(C_3^x) = 0.345\,88\,(22)$, and $q_3 = 0.006\,42(25)$, all in cm^{-1} with one standard deviation in parentheses. The transition frequencies and the molecular constants of the ν_3 band may be useful in a search for interstellar CH_3 .

I. INTRODUCTION

Calculations of the molecular evolution of dark clouds in the interstellar medium have shown that CH_3 may be one of the most abundant free radicals.^{1,2} Since the CH_3 radical is a planar molecule,^{3,4} no rotational transitions in the millimeter or far-infrared region are expected, except possible $\Delta K = \pm 3$ transitions induced by the centrifugal distortion.⁵ The known electronic transitions of CH_3 are diffuse and lie in the vacuum ultraviolet region.⁴ The observation of the infrared vibration-rotation transitions is thus a more promising way of detecting this species in interstellar space.

Recently Yamada, Hirota, and Kawaguchi³ observed the ν_2 band (out-of-plane bend) of CH_3 at high resolution in the $16\,\mu\text{m}$ region. They estimated that the transition moment is as large as $0.1\,\text{D}$ which is comparable to that of the ν_2 band of NH_3 ($0.24\,\text{D}$). Unfortunately, the ν_2 band of CH_3 is overlapped by the ν_2 band of CO_2 and therefore ground based observation at $16\,\mu\text{m}$ is not very favorable for the detection of extraterrestrial CH_3 .

The ν_3 band (the in-plane degenerate CH stretch) was estimated to lie near $3162\,\text{cm}^{-1}$ on the basis of the infrared spectra of matrix isolated CH_3 .^{6,7} In the present paper we report the observation of the high-resolution absorption spectrum of the ν_3 band of CH_3 recorded with a difference frequency laser spectrometer. The ν_3 band lies in the $3\,\mu\text{m}$ atmospheric window region and thus a search for interstellar CH_3 using this band seems promising. The transition frequencies reported here may prove useful for such a search.

II. EXPERIMENTAL

The experimental apparatus was described in a previous paper on NH_2 .⁸ Briefly, tunable infrared laser radiation was generated by mixing the output of an Ar^+ laser with radiation from a dye laser. The following two modifications were made after the NH_2 work: (1) a ring dye laser (CR 699-21) was installed and (2) the Zeeman modulation cell was improved. In a new cell, the maximum available modulation field was increased

to $550\,\text{G}$ (peak-to-peak).

The CH_3 radical was produced by discharging $[(\text{CH}_3)_3\text{CO}]_2$ (di-tert-butylperoxide), CH_4 , CH_3CN , or CH_3OH . When $[(\text{CH}_3)_3\text{CO}]_2$ was used as a starting material, a mild ac discharge was favorable. The secondary output of a neon-sign transformer at $7\,\text{kV}$ was applied to the electrodes. A dc discharge with about $35\,\text{mA}$ current was used for CH_4 , CH_3CN , or CH_3OH . The optimum reaction conditions did not depend critically on the pressure. In most measurements, the pressure was about 0.6 to $1\,\text{Torr}$.

All the starting materials cited above yielded about the same concentration of the CH_3 radical. However, a discharge in CH_4 or CH_3CN gave a less congested absorption spectrum and made it possible to observe several transitions with frequency modulation. This was particularly important for CH_3 , because the Zeeman effect was generally very small.

The transition wave numbers were calibrated with the absorption lines of C_2H_4 ⁹ or NH_3 .¹⁰ Relative frequency markers of $0.01\,\text{cm}^{-1}$ spacing were provided by a confocal Fabry-Perot etalon.

III. RESULTS AND DISCUSSIONS

A. Assignment

A series of lines were found in the 3148 – $3155\,\text{cm}^{-1}$ region. The wave numbers were fit to the following equation:

$$\nu(N) = \nu_{\text{sub}} - \alpha^B N(N+1), \quad (1)$$

with $N = 2, 4, 6$, and 8 . We assigned these lines as ${}^{\infty}Q_0(N)$ for the following reasons. (1) Since the CH_3 radical is planar and the symmetry of the ground electronic state is ${}^2A_2''$, the levels with $K = 0$ and $N = \text{odd}$ are missing. (2) These lines are the strongest of the Zeeman modulated lines. Simulation of the Zeeman modulated line profile supported this assignment. (3) The α^B constant ($\sim 0.100\,\text{cm}^{-1}$) agrees well with the predicted value from a force field calculation.¹¹ Subse-

quently, another series of Q -branch lines $^pQ_1(N)$ with $N=1-5$ was assigned. Eventually 47 lines were assigned, and three Zeeman-modulated lines remained unassigned.

The spin-rotation splittings were not resolved, but the Zeeman modulated line shape was affected by the unresolved spin-rotation splitting. The transition frequencies of the Zeeman modulated lines were corrected

TABLE I. Observed wave numbers (in cm⁻¹) of the transitions of the ν_3 band of CH₃.

$N'K'$	NK	obs	o-c ($\times 10^4$)
3 1	4 0	3077.6321	41
1 1	2 0	3116.8529	-22
4 4	4 3	3123.2102	10
2 2	3 3	3128.5472	9
4 3	4 2	3133.1270	42
3 3	3 2	3133.9232	8
1 1	2 2	3137.5637 ^a	3
8 1	8 0	3148.1247	-7
6 1	6 0	3151.1089 ^a	18
4 1	4 0	3153.3250 ^a	17
2 1	2 0	3154.7468	3
5 0	5 1	3162.4246 ^a	15
4 0	4 1	3163.4976	-11
3 0	3 1	3164.3601 ^a	-8
2 0	2 1	3165.0069	-16
1 0	1 1	3165.4384	-24
6 1	6 2	3171.4611 ^a	-15
5 1	5 2	3172.7826 ^a	10
4 1	4 2	3173.8797 ^a	-36
1 1	0 0	3174.2935 ^a	-12
2 1	2 2	3175.4285	-10
2 2	1 1	3182.8613 ^a	-7
4 2	4 3	3184.4284	68
3 2	3 3	3185.3244	-8
5 3	5 4	3193.9738	-9
4 3	4 4	3195.1295	18
3 2	2 1	3201.3468	12
6 4	6 5	3203.4231	-31
5 4	5 5	3204.8392	18
4 3	3 2	3209.5916 ^a	-7
8 5	8 6	3210.8693	43
3 1	2 0	3211.4424	42
7 5	7 6	3212.7726	-45
6 5	6 6	3214.4567	19
5 4	4 3	3217.7548 ^a	4
3 0	2 1	3221.7497	-35
8 6	8 7	3222.0272	-15
7 6	7 7	3223.9812	3
6 5	5 4	3225.8321 ^a	-7
5 3	4 2	3227.5728 ^a	-8
7 6	6 5	3233.8207 ^a	-81
6 4	5 3	3235.4925 ^a	5
5 2	4 1	3237.5157 ^a	-2
4 0	3 1	3239.9319	-37
8 7	7 6	3241.7486 ^a	44
6 3	5 2	3245.2667 ^a	10
5 1	4 0	3247.4863 ^a	-11

^aMeasured with frequency modulation. All other lines were measured with Zeeman modulation, and the transition wave numbers were corrected for the Zeeman shifts (see the text).

TABLE II. Molecular constants of CH₃ in the ν_3 state (in cm⁻¹).

	$\nu_3 = 1$	Ground state ^a
ν_0	3160.821 2(12) ^b	
B	9.471 10(14)	9.577 89
C	4.701 67(15)	4.742 75
$D_N \times 10^3$	0.759 0(37)	0.770
$D_{NK} \times 10^3$	-1.366(11)	-1.358
$D_K \times 10^3$	0.637 1(95)	0.634
$C\zeta$	0.345 88(22)	
$\eta_N \times 10^3$	-0.121(21)	
$\eta_K \times 10^3$	0.151(29)	
q_3	0.006 42(25)	
$q_N \times 10^3$	0.029 6(71)	

^aReference 3.

^bOne standard error to the last digits of constants.

by the line simulation method that will be described in detail in the following section. Table I lists the corrected wave numbers of the assigned lines together with the residuals of the least-squares fit.

The energy levels in the excited vibrational state were calculated using the following matrix elements:

$$\begin{aligned} \langle Nkl | H_{vr}^0 | Nkl \rangle = & \nu_3^0 + BN(N+1) + (C-B)k^2 - D_N N^2(N+1)^2 \\ & - D_{NK} N(N+1)k^2 - D_K k^4 - kl[2(C\zeta)_3 - \eta_N N(N+1) - \eta_K k^2], \end{aligned} \quad (2)$$

$$\begin{aligned} \langle N, k+1, l=1 | H_l | N, k-1, l=-1 \rangle = & \frac{1}{2} [q_3 + q_N N(N+1)] \\ & \times \{ [N(N+1) - k(k-1)][N(N+1) - k(k+1)] \}^{1/2}. \end{aligned} \quad (3)$$

Several preliminary fits were made to establish which molecular parameters could be reliably determined. Introduction of the four H parameters H_N , H_{NK} , H_{KN} , and H_K improved the variance of the fit slightly but our data set was not extensive or accurate enough to reliably determine them. The final molecular constants of Table II were obtained with the H 's set to zero. The molecular constants in the ground state were fixed at the values determined by Yamada, Hirota, and Kawaguchi.³

B. Zeeman modulation

The spin-rotation splittings of a given rotational level N_K are given by

$$\Delta\nu_{sr} = - (N + \frac{1}{2}) \{ \epsilon_{bb} - (\epsilon_{bb} - \epsilon_{cc}) K^2 / [N(N+1)] \}, \quad (4)$$

where $\epsilon_{bb} \simeq -350$ MHz and $\epsilon_{cc} \simeq -3$ MHz in the ground state.¹² The splittings in the ν_3 excited state are comparable to those in the ground state. Therefore, for most transitions in the ν_3 band, the spin-rotation doubling is comparable to, or smaller than the Doppler width (the half-width is about 200 MHz at 500 K). The electron spin is decoupled from molecular rotation at a few hundred G, and the electric dipole allowed transitions lose tunability. Because of this decoupling effect (Paschen-Back effect), Zeeman modulation is inefficient for most transitions in the ν_3 band of CH₃.

The spin-rotation splittings for each rotational level N_K are plotted in Fig. 1. By assuming that the values for ϵ_{bb} and ϵ_{cc} are the same in the ν_3 as in the ground state, this figure can be used to illustrate the difference

in the spin-rotation splittings between the upper and the lower states involved in a particular transition. The arrows each connect a point with ground state quantum number N_K to a point with upper state quantum number N'_K , and they indicate the transitions successfully observed by Zeeman modulation. The strong ${}^{\circ}R_N(N)$ and ${}^{\circ}P_N(N)$ lines have not been observed by Zeeman modulation [with the exception of the first member of the series ${}^{\circ}R_0(0)$], and these transitions are represented by the almost horizontal lines at the bottom of the figure. They have the smallest spin-rotation splittings and the smallest differences in splittings. Most Q-branch lines, indicated by vertical arrows in Fig. 1, with the difference in splittings either less than 170 MHz or greater than 360 MHz have been observed.

The line shape of the Zeeman modulated transitions depends on the size of the spin-rotation splittings. Figure 2 shows some typical examples of the line shapes. These differences in the line shape were well accounted for by line profile simulation as illustrated in Fig. 2.

The Zeeman modulated line profile was calculated, using the following equation:

$$S(\nu) = \frac{1}{n} \sum_{i=1}^n \sum_m I_{im} \cos \theta_i \cdot f(\nu, \nu_{im}) . \quad (5)$$

One cycle of the modulation was divided into n divisions. The center frequency ν_{im} was calculated for the i th division of the modulation and for a particular $m (=M_N)$ component (in the present experiment, the selection rule was $\Delta M_N = \pm 1$). A Doppler broadened line profile was as-

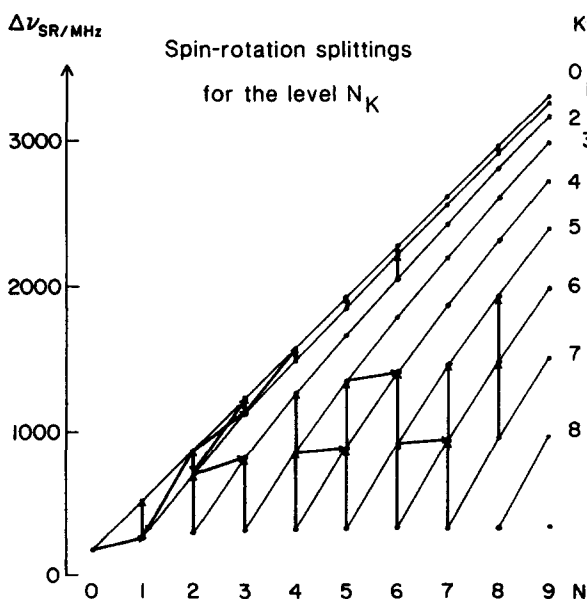


FIG. 1. The spin-rotation splittings for the rotational level N_K . The thin line connects the points of the same K quantum number. The arrows each connect a point with ground state quantum number N'_K to a point with upper state quantum number N_K . For example, the arrow in the lower left hand corner of the figure indicates the $1_1 \leftarrow 0_0$ transition. The difference of the vertical scale between the two points connected by an arrow indicates approximately the difference in the spin-rotation splittings between the upper and the lower state.

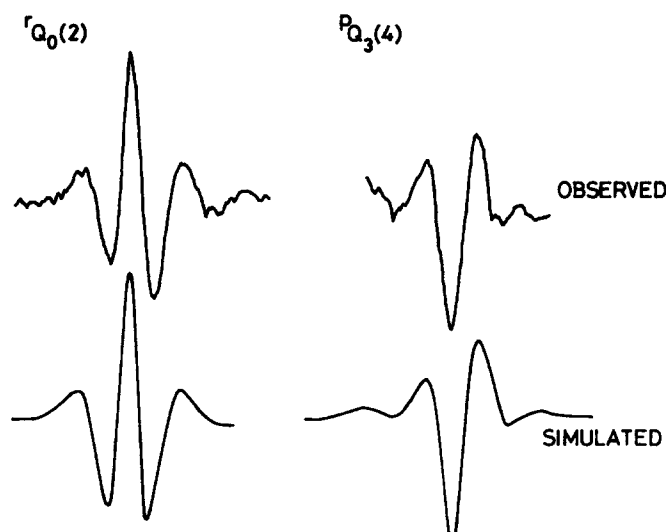


FIG. 2. Examples of observed and simulated line shapes. These traces were recorded with the modulation amplitude of 200 G (peak-to-peak) and the dc field of 200 G.

sumed for all the M_N components

$$f(\nu, \nu_{im}) = \exp[-\ln 2 \cdot (\nu - \nu_{im})^2 / (\Delta\nu_D)^2] . \quad (6)$$

The relative intensity I_{im} was calculated for each m and also for each division of the modulation, because the mixing between the two spin-rotation components varies during one cycle of modulation. In Eq. (5), θ_i is equal to $2\pi i/n$, and $\cos \theta_i$ is the response function of a lock-in amplifier. The number of divisions n was usually taken to be 10. We found that the final line shape did not change appreciably by increasing the number of divisions from 10 to 20.

The modulation efficiency, which is defined as the ratio of the peak-to-peak intensity calculated with Eq. (5) to the line strength at the zero field, is only 14% at most. Although Zeeman modulation was inefficient, it was vital for the observation of the relatively weak lines of the CH₃ among other much stronger diamagnetic lines due to the parent molecule and other reaction products. At a later stage of the experiment, source modulation was used in a discharge of CH₄ or CH₃CN for the observation of some lines that could not be observed with Zeeman modulation. However, this was possible only by using good predictions of the transition frequencies provided by the analysis of the lines already obtained by Zeeman modulation.

C. Molecular constants

The band origin ($\nu_0 = 3160.8212 \text{ cm}^{-1}$) agrees well with the values obtained from the matrix isolation experiments 3162 cm^{-1} in Ne⁶ and 3150 cm^{-1} in Ar⁷ matrices.

The vibration-rotation constants α_3^B and α_3^C were determined for the first time. They agree very well with the values ($\alpha_3^B = 0.10024$ and $\alpha_3^C = 0.03921 \text{ cm}^{-1}$) estimated from a force field calculation.¹¹ The first order Coriolis coupling constant ξ_3 was estimated to be 0.0736 by dividing the value of $(C\xi)_3$ by C_3 , and in Ref.

11 the value 0.0858 was obtained for ζ_3 .

The sign of the l -type doubling constant q_3 was determined by observing the shifts of the A_2 components of the l -type doublet of the $K=l=1$ levels (the other components A_1 are nonexistent in CH₃). It was found from the staggering of the A_2 levels that they lie lower than the A_1 components for the level with even N and vice versa for the level with odd N . The l -type doubling constant is given by¹³

$$q_3 = -\frac{2B^2}{\nu_3} \left\{ \frac{3\nu_3^2 + \nu_2^2}{\nu_3^2 - \nu_2^2} (\zeta_{23}^{(v)})^2 + (\text{anh}) \right\}, \quad (7)$$

where (anh) means the anharmonic contribution. The harmonic part of Eq. (7) was calculated to be

$$q_3(\text{harmonic}) = -0.08052 \text{ cm}^{-1}. \quad (8)$$

The experimental value for q_3 is 0.0064 cm⁻¹. Therefore, the anharmonic part of q_3 makes a substantial contribution to the constant.

Snelson⁶ found the absorbance ($\log I_0/I$) of the ν_2 and ν_3 fundamental bands to be 0.4 and 0.05, respectively, for CH₃ in a neon matrix. This implies that the ratio of the transition dipole moments $|\mu_2/\mu_3| \sim 2.8$. Therefore, if we assume $|\mu_2| = 0.1 \text{ D}$, we obtain $|\mu_3| = 0.036 \text{ D}$. This value leads to a determination of the average concentration of CH₃ in the present experiment to be 4×10^{13} molecules/cm³, where we estimated the minimum detectable absorption coefficient to be 6×10^{-7}

cm⁻¹. This concentration of the radical is consistent with the estimate by Yamada, Hirota, and Kawaguchi from the observation of the ν_2 band.³

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