JOURNAL OF MOLECULAR SPECTROSCOPY 25, 224-239 (1968)

Vibration-Rotation Bands of ¹³CH₃Cl

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The two parallel fundamental bands, ν_2 and ν_3 , and the three perpendicular fundamental bands, ν_4 , ν_5 and ν_6 in the infrared spectrum of ${}^{13}\text{CH}_3\text{Cl}$ have been studied at high resolution and analyzed in detail. Isotopic splitting, due to ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$ present in natural abundance in the sample, has been observed in the ν_2 and ν_3 bands and the centers of the ${}^{13}\text{CH}_3{}^{37}\text{Cl}$ bands located. The anomalous Q branch intensity alternation in the ν_4 perpendicular band, which has also been reported in the spectrum of ${}^{12}\text{CH}_3\text{Cl}$, is attributed to a Fermi resonance interaction between ν_4 and $3\nu_6$, which are almost exactly accidentally degenerate. An analysis in terms of this Fermi resonance has been performed and the molecular constants and band center for ν_4 determined. Vibration frequencies and rotational constants of ${}^{13}\text{CH}_3\text{Cl}$ determined in this work and elsewhere are summarized in Table VII. Finally, a re-analysis of the ν_4 band of ${}^{12}\text{CH}_3\text{Cl}$ in terms of a Fermi resonance with $3\nu_6$ is performed.

INTRODUCTION

The infrared and microwave spectra of ¹²CH₃Cl have been subjected to fairly thorough investigation by a number of workers, and most of the spectrum is now well understood. (See Refs. 1 and 2, and further references therein.) However, little information is available about the isotopic molecule ¹³CH₃Cl, except that obtained from microwave studies on this molecule in its natural abundance of 1% (3). The preparation of a sample of CH₃Cl enriched in ¹³C in this laboratory provided the material for an investigation of its infrared spectrum. This paper reports the results obtained from high resolution analyses of the parallel fundamentals, ν_2 and ν_3 , and of the perpendicular fundamentals, ν_4 , ν_5 , and ν_6 .

EXPERIMENTAL PROCEDURE

The sample of methyl chloride was prepared by reaction of 57 % ¹³C enriched methanol with aluminium trichloride (4). The reaction mixture was maintained at 50°C *in vacuo* for 1 hour, and then at about 140°C for 2 hours under a slow stream of N₂, the products being collected in low temperature traps. Repeated passage of the products through KOH pellets removed HCl, and the sample was distilled from an acetone/CO₂ bath to remove any traces of H₂O. The product, obtained in 80 % yield, revealed no impurity bands in the infrared spectrum, and appeared to contain ~57 % ¹³CH₃Cl. Spectra were recorded on a Perkin–Elmer

| (CM ⁻¹ in vacuo) | | | | |
|-----------------------------|------------|----|------------|--|
| K | $^{Q}Q(K)$ | K | $^{Q}Q(K)$ | |
| 3 | 2963.84 | 9 | 2959.74 | |
| 5 | 2962.96 | 10 | 2958.68 | |
| 6 | 2962.33 | 11 | 2957.42 | |
| 7 | 2961.55 | 12 | 2956.02 | |
| 8 | 2960.69 | | | |

TABLE I

Q BRANCH LINE FREQUENCIES OF THE ¹⁸CH₃Cl ν_1 Fundamental (Cm⁻¹ in vacuo)

225 double-beam, grating infrared spectrometer using a Golay detector and additional recording apparatus. The resolving power was $\sim 0.3 \text{ cm}^{-1}$ at 3000 cm⁻¹ and $\sim 0.2 \text{ cm}^{-1}$ elsewhere. Ten cm cells were used throughout. Compensation of ¹²CH₃Cl in the sample was effected by placing in the reference beam a cell connected to a mobile grid and into which any desired pressure of ¹²CH₃Cl could be introduced. At the outset, it was not known how effective such a method of compensation would be. In the perpendicular bands, no apparent difficulties were experienced with regard to the Q branch contours, although the rotational Jstructure could not be satisfactorily resolved in any of the bands. In the parallel bands, the rotation lines could be resolved readily in bands below 2000 cm⁻¹, and the effects of ³⁷Cl lines observed, although the majority of lines suffered a certain amount of distortion.

The spectra of CH₄, HCl, H₂O, NH₃ and CO₂ were used as secondary standards to calibrate the spectrometer, wavenumber data being taken from the I.U.P.A.C. tables, supplemented by further data from references therein where necessary. All reported line positions are the average of a number of runs, and it is estimated that the internal consistency of our results is ± 0.02 to ± 0.03 cm⁻¹, except in the region of 3000 cm⁻¹, where it is ± 0.05 cm⁻¹. Some difficulty was experienced in measuring up lines accurately; owing to their distortion due to the overlapping of the compensated spectrum of ¹²CH₃Cl, and of the spectrum of ¹³CH₃³⁷Cl in natural abundance.

RESULTS AND ANALYSES

A. PARALLEL BANDS

(I) ν_1 , 2964 cm^{-1}

It was not possible to resolve the parallel fundamental ν_1 at 2964 cm⁻¹ well enough in order to perform a satisfactory rotational analysis. As with the corresponding band in ¹²CH₃Cl, however, the Q branch exhibits a very pronounced K-splitting, with the lines due to K = 3, 6, and 9 dominant. The observed line positions are given in Table I. Assuming that α_1^{B} is very small (-0.0001 cm⁻¹

| (CM + in vacuo) | | | | | | | | | |
|-----------------|---------|-------|---------|-------|----|---------|-------|---------|-------|
| J | R(J) | Calc | P(J) | Calc | J | R(J) | Calc | P(J) | Calc |
| 3 | 1352.74 | 52.75 | | | 19 | 1364.88 | 4.89 | 1331.89 | 1.86 |
| 4 | 53.55 | 3.57 | | | 20 | 65.60 | 5.58 | 30.89 | 0.87 |
| 5 | 54.35 | 4.38 | | | 21 | 66.30 | 6.27 | 29.87 | 29.86 |
| 6 | | 5.18 | | | 22 | 66.98 | 6.94 | 28.85 | 8.85 |
| 7 | 55.99 | 5.97 | 1343.25 | 43.28 | 23 | 67.64 | 7.61 | 27.84 | 7.82 |
| 8 | 56.77 | 6.76 | 42.33 | 2.37 | 24 | 68.26 | 8.27 | 26.80 | 6.79 |
| 9 | 57.54 | 7.54 | 41.44 | 1.46 | 25 | 68.92 | 8.92 | 25.75 | 5.75 |
| 10 | 58.37 | 8.30 | 40.52 | 0.54 | 26 | 69.57 | 9.58 | 24.70 | 4.71 |
| 11 | 59.10 | 9.07 | 39.56 | 39.60 | 27 | 70.18 | 70.22 | 23.70 | 3.65 |
| 12 | 59.83 | 9.82 | | 8.67 | 28 | 70.82 | 0.85 | 22.65 | 2.59 |
| 13 | 60.57 | 60.57 | 37.71 | 7.71 | 29 | 71.45 | 1.48 | 21.60 | 1.51 |
| 14 | 61.30 | 1.30 | 36.74 | 6.77 | 30 | 72.07 | 2.09 | 20.55 | 0.44 |
| 15 | 62.04 | 2.04 | 35.81 | 5.80 | 31 | 1372.65 | 2.70 | 19.43 | 19.35 |
| 16 | 62.80 | 2.77 | 34.82 | 4.83 | 32 | | | 18.27 | 8.26 |
| 17 | 63.49 | 3.48 | 33.88 | 3.85 | 33 | | | 1317.17 | 7.16 |
| 18 | 1364.22 | 4.19 | 1332.88 | 2.86 | | | | | |
| | | | | | | | | | |

TABLE II LINE FREQUENCIES OF THE ¹³CH₃Cl ν_2 FUNDAMENTAL

in ν_1 of ¹²CH₃Cl), the Q branches of the K sub-bands may be analyzed approximately in terms of the equation

$${}^{Q}Q_{K} = \nu_{0} + (A' - A'')K^{2},$$

from which it is found that $\nu_0 = 2964.38 \text{ cm}^{-1}$, and $\alpha_1^A = +0.0576 \text{ cm}^{-1}$.

(II) ν_2 , 1349 cm^{-1}

This band proved to be somewhat difficult to measure up on account of the distortion of many of the 35 Cl rotation lines by underlying weaker lines due to the natural abundance of 13 CH $_{3}^{37}$ Cl in the sample. Also, the compensation in the reference beam of the $\sim 45 \% {}^{12}$ CH $_{3}$ Cl in the sample caused distortion of many of the line contours. The averaged line positions from several runs are listed in Table II.

No evidence of K-splitting was observed in any part of the band. It was found that the errors associated with the line positions were too large for any effects of centrifugal distortion to be discerned, and so an analysis was performed in terms of the equation for a parallel band

$${}^{Q}P, R(J) = \nu_{0} + (B' + B'')m - (B' - B'')m^{2}$$

in which m = -J for the P branch and m = J + 1 for the R branch. From a least-squares treatment of the combination difference relations, and a plot of

 $(R_{J-1} + P_J)$ against J^2 , the following results were obtained

$$B'' = 0.4271 \pm 0.0004 \text{ cm}^{-1},$$

$$B' = 0.4234 \pm 0.0005 \text{ cm}^{-1},$$

$$\nu_0 = 1349.42 \pm 0.03 \text{ cm}^{-1},$$

$$\alpha_2^{\ B} = +0.00383 \pm 0.00006 \text{ cm}^{-1}.$$

The value for B'' agrees fairly well with the microwave value of 0.42684 cm⁻¹ (3, 5), considering the difficulty experienced in measuring up the J lines. As would be expected for the small mass change ¹²C to ¹³C, the rotational constant α_2^B is closely similar to that found by Holladay and Nielsen for the corresponding band in ¹²CH₃Cl (1).

The observed line positions should best be reproduced by the equation

$${}^{Q}P, R(J) = 1349.42 + 0.8505m - 0.00383m^{2},$$

and the values calculated using this equation are compared with the observed values in Table II. On the whole, the agreement is satisfactory.

From the distortions produced in the ³⁵Cl lines, the approximate positions of the ³⁷Cl lines can be assessed. Almost exact coincidences of lines from the two isotopic molecules appear to occur between P(23) and P(27) and between R(21) and R(24) in the observed spectrum of ¹³CH₃³⁵Cl. Using the microwave value of $B'' = 0.41996 \text{ cm}^{-1}$ (3) for ¹³CH₃³⁷Cl, and the same value for α_2^{B} as determined above, the observed effects of the underlying ³⁷Cl lines were best reproduced with the band center of ν_2 for ¹³CH₃³⁷Cl located at 1349.09 cm⁻¹. This gives a separation between the two band centers of 0.34 cm⁻¹; Holladay and Nielsen obtained a value of 0.27 cm⁻¹ for the corresponding band center separation in the ¹²C molecules (1).

$(III) \nu_3, 715 \ cm^{-1}$

This band, mainly associated with the stretching of the C–Cl bond, was well resolved and the two series of J lines arising from the ³⁵Cl and ³⁷Cl isotopic species were easily discerned in the spectrum, although actual isotopic splitting was observed only at a few points. Due to the compensation of ¹²CH₃Cl in the reference beam, the J lines suffer some distortion, and are not observable at all in the region of the Q branch of ν_3 for ¹²CH₃Cl. No evidence of any K-splitting was observed in the band, which exhibits a marked degradation towards lower wave numbers.

The rotation line positions due to ${}^{13}\text{CH}_3^{35}\text{Cl}$ were fairly readily measured in this band, allowance being made for the effects of underlying lines due to ${}^{13}\text{CH}_3^{37}\text{Cl}$. The measured values are quoted in Table III; values in parentheses are for lines which were particularly distorted and hence which may be less reliable. A com-

| J | R(J) | Calc | P(J) | Calc | J | R(J) | Calc | P(J) | Calc |
|-----------|----------|-------|---------|-------|-----------|----------|-------|--------|-------|
| 3 | 718.21 | 18.22 | | | 20 | (731.00) | 31.07 | 696.41 | 96.43 |
| 4 | 19.06 | 9.04 | _ | | 21 | | 1.76 | 95.41 | 5.44 |
| 5 | 19.88 | 9.85 | | | 22 | | 2.44 | 94.45 | 4.43 |
| 6 | 20.68 | 20.65 | 709.69 | 09.65 | 23 | | 3.11 | 93.46 | 3.42 |
| 7 | 21.47 | 1.45 | 08.79 | 8.76 | 24 | - | 3.77 | 92.44 | 2.40 |
| 8 | 22.25 | 2.23 | 07.88 | 7.85 | 25 | (34.38) | 4.43 | 91.37 | 1.37 |
| 9 | 23.01 | 3.01 | 06.93 | 6.94 | 26 | 35.07 | 5.07 | 90.36 | 0.34 |
| 10 | 23.81 | 3.78 | (06.03) | 6.02 | 27 | 35.74 | 5.71 | 89.33 | 89.30 |
| 11 | 24.55 | 4.54 | (05.13) | 5.09 | 28 | 36.38 | 6.35 | 88.29 | 8.25 |
| 12 | 25.30 | 5.30 | 04.17 | 4.16 | 29 | 37.01 | 6.97 | 87.23 | 7.20 |
| 13 | 26.03 | 6.05 | 03.22 | 3.22 | 30 | 37.61 | 7.59 | 86.17 | 6.14 |
| 14 | 26.79 | 6.79 | 02.26 | 2.27 | 31 | 38.20 | 8.19 | 85.09 | 5.07 |
| 15 | 27.55 | 7.52 | 01.31 | 1.32 | 32 | 38.84 | 8.80 | 84.01 | 4.00 |
| 16 | 28.29 | 8.25 | 700.33 | 0.35 | 33 | 39.47 | 9.39 | 82.92 | 2.92 |
| 17 | 28.99 | 8.96 | 699.38 | 99.38 | 34 | 740.05 | 9.97 | 81.85 | 1.83 |
| 18 | 29.67 | 9.67 | 98.42 | 8.41 | 35 | | | 680.78 | 0.73 |
| 19 | (730.32) | 30.38 | 697.43 | 7.42 | | | | | |

TABLE III LINE FREQUENCIES OF THE ¹³CH₃Cl ν_3 FUNDAMENTAL (CM⁻¹ in vacuo)

plete analysis including centrifugal distortion terms was possible in this case, and the rotational constants were determined graphically from the relevant combination sum and difference relations (6). The results obtained were

$$\begin{split} \nu_0 &= 714.88_5 \pm 0.03 \ \mathrm{cm}^{-1}, \\ v_3 &= 0 \begin{cases} (B - D_{JK}\bar{K}^2) &= 0.42677 \pm 0.00030 \ \mathrm{cm}^{-1}, \\ 10^7 D_J &= 7.6 \pm 1.2 \ \mathrm{cm}^{-1}, \\ v_3 &= 1 \begin{cases} (B - D_{JK}\bar{K}^2) &= 0.42295 \pm 0.00030 \ \mathrm{cm}^{-1}, \\ 10^7 D_J &= 6.5 \pm 1.2 \ \mathrm{cm}^{-1} \\ \alpha_3^{\ B} &= +0.00370 \pm 0.00005 \ \mathrm{cm}^{-1}, \\ \alpha_3^{\ A} &\coloneqq \alpha_3^{\ B}, \text{ (assumed on the evidence of no observa ble K-splitting).} \end{split}$$

Due to the compensation of the spectrum of ¹²CH₃Cl present in the sample and the resulting distortion to some of the lines, there was a fair scatter of points in the graphs, which gave rise to the rather large errors associated with the values of D_J . Only the combined value of $(B - D_{JK}\bar{K}^2)$ can be obtained from such an analysis where the K-splitting is not observed and measurable. \bar{K}^2 is some effective average value of K which depends on the intensity distribution over the sub-bands. A comparison of the observed ground state value with the microwave values for B'' and D''_{JK} (assumed to be the same as for ¹²CH₃Cl) suggests that $\bar{K}^2 = 10$, or that $\bar{K} = 3$, a value which agrees exactly with that calculated by Holladay and Nielsen to predict the maximum of any J 'line' for $J \ge 11$ in the ν_3 band of ¹²CH₃Cl. This agreement, however, may be somewhat fortuitous, considering the scatter of points in our graphical analysis.

The observed P and R line positions of ν_3 (¹³CH₃³⁵Cl) are best reproduced using the equation

 ${}^{Q}P, R(J, \bar{K}) = 714.885 + 0.8497m - 3.7 \times 10^{-3}m^{2} - 2.8 \times 10^{-6}m^{3},$

where m = -J for the P branch, or J + 1 for the R branch. The observed and calculated line positions are compared in Table III.

The corresponding band due to ν_3 of ${}^{13}\text{CH}_3{}^{37}\text{Cl}$ could not be analysed in the same manner, as the *P* and *R* branch line positions could not be measured to a sufficiently high accuracy. However, reasonable estimates of the line positions could be made and the *Q* branch was readily observed in the spectrum approximately 6 cm⁻¹ lower than that of ${}^{13}\text{CH}_3{}^{35}\text{Cl}$. Using the microwave value for B'' of 0.41996 cm⁻¹ and α_3^{B} as found for ${}^{13}\text{CH}_3{}^{35}\text{Cl}$, and ignoring centrifugal distortion effects, the estimated line positions were best fitted with the band center of ν_3 for ${}^{13}\text{CH}_3{}^{37}\text{Cl}$ located at 708.98 \pm 0.05 cm⁻¹.

The only other parallel band of reasonable intensity observed in the spectrum was that of the parallel component of $2\nu_5$, which is in Fermi resonance with ν_1 . However, the contour of this band was not resolved well enough to merit an analysis.

- B. PERPENDICULAR BANDS
 - (1) ν_4 , 3030 cm⁻¹

This band, associated almost entirely with the degenerate stretching motions of the CH bonds, exhibits the characteristic pattern of a perpendicular band of a series of well resolved Q branches on a background of weaker absorptions. As observed in the corresponding band in ¹²CH₃Cl, the usual three-fold intensity alternation of the Q branches becomes upset near the band center, the Q branches broaden considerably and the spacing between the Q branches becomes smaller than that in the wings of the band. Although a Coriolis interaction with the nearby parallel vibration, ν_1 , is possible, it would not be expected to cause a localized effect such as this, but rather would exert an intensity perturbation over the whole band (7). It is doubtful, in any case, if such an interaction would be observable in this case, since the Coriolis zeta constant between different hydrogen stretching motions is always close to zero, and this constant controls the magnitude of the interaction. The most likely cause of the observed effect lies in the observation that $3\nu_6$ will occur at almost exactly the same frequency as ν_4 ,



and that the perpendicular component of $3\nu_6$ is in Fermi resonance with ν_4 . This is a second order Fermi resonance, the effect of which would be expected to be small and only observable around the point of resonance. What is being observed, therefore, is two series of Q branches, each dying away rapidly on one side of its band center, and which will be analyzable in terms of a Fermi resonance between ν_4 and $3\nu_6$ (8,9). The overall appearance of the band is shown in Fig. 1, and the observed Q branch maxima positions are listed in Table IV. Figure 2 shows a plot of Q branch position against m, where m = +K for the ${}^{R}Q_{K}$ branches and m = -K for the ${}^{P}Q_{K}$ branches. From such a plot the numbering of the Q branches is relatively easy, since one must be in error by an integral multiple of 3 due to the intensity alternation, and only one set of numbering will be reasonable and consistent with the overall band contour. In the case of this band we think that we can observe the weak ${}^{R}Q_{K}$ branches of the lower wave number component up to K = 6. The corresponding weak ${}^{P}Q_{K}$ branches of the higher wave number component are not observable, due to overlapping of the band by the R branch of ν_1 .

In terms of the Fermi resonance interaction term W, the perturbed Q branch frequencies are given by the equation (9, 10)

$$\nu^{\pm} = \frac{1}{2}(\nu_4 + \nu_{666}) \pm \frac{1}{2}[(\nu_4 - \nu_{666})^2 + 4W^2]^{1/2}, \tag{1}$$

where

$$\nu_{i} = \nu_{i}^{0} + [A_{i}'(1-\zeta_{i})^{2} - B_{i}'] + 2[A_{i}'(1-\zeta_{i}) - B_{i}']m + [(A_{i}' - A'') - (B_{i}' - B'')]m^{2},$$
(2)

| (CM ⁻¹ in vacuo) | | | | | |
|-----------------------------|------------------------------|-----------------|--|--|--|
| mª | $ u^+ $ | ν | | | |
| 12 | 3134.65 | | | | |
| 11 | 3126.16 | | | | |
| 10 | 3118.72 | | | | |
| | 3111.55 | | | | |
| 9 | 3110.75 triplet ^b | | | | |
| | 3109.85 | | | | |
| 8 | 3101.90 doublet ^b | | | | |
| | 3101.19 | | | | |
| 7 | 3093.34 | | | | |
| 6 | 3085.13 | 3071.3 | | | |
| 5 | 3076.83 | 3064.0 | | | |
| 4 | 3068.34 | 3056.5 | | | |
| 3 | 3059.91 | 3048.8 | | | |
| 2 | 3051.40 | 3041.2 | | | |
| 1 | 3042.95 | 3034.43 | | | |
| 0 | 3034.43 | 3026.11 | | | |
| 1 | 3026.11 | 3017.88 broad | | | |
| -2 | 3017.88 broad | 3010.31 v broad | | | |
| 3 | 3010.31 v broad | 3003.29 | | | |
| | 3003.29 | 2994.36 | | | |

TABLE IV Q BRANCH FREQUENCIES OF THE ¹³CH₃Cl ν_4 and $3\nu_6$ Fermi Diad (cm⁻¹ in vacuo)

* The m = +K for the ${}^{R}Q_{K}$ branches, m = -K for the ${}^{P}Q_{K}$ branches.

^b The RQ_8 and RQ_9 in ν^+ are definitely perturbed. Each is split, RQ_8 into two components and RQ_9 into three components. RQ_9 is less intense than its neighboring Q branches, and the Q branch spacings are erratic in this region. The cause of the local perturbation is not known.

and m in the latter equation of the unperturbed bands is +K for the ^{*R*}*Q* and -K for the ^{*P*}*Q* branches. The effect of the term in *W* is to cause the *Q* branches to be pushed further apart near the resonance point, thus affecting the *Q* branch spacing.

Provided enough Q branches are measurable to a sufficiently high accuracy, all the constants in Eqs. (1) and (2) may be solved by a least-squares calculation (9). If this is not the case, as in the present case, much useful information can be obtained from the equations. A plot of Q branch spacing against running number m (m = +K for the ${}^{R}Q_{\kappa}$ branches, m = -K for the ${}^{P}Q_{\kappa}$ branches) for the main series of branches will show up the resonance clearly and should be asymptotic to a straight line of slope 2[(A' - A'') - (B' - B'')] and intercept at m = 0 of $2[A'(1 - \zeta) - B']$, thus enabling a value of ζ to be calculated. (If both series of Q branches are observable, it should be possible to carry this out for each series.) In the present case, for unperturbed ν_4 , we find

$$[(A' - A'') - (B' - B'')] = -0.025 \text{ cm}^{-1}$$

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F1G. 2. The observed Q branch positions (\odot) and the asymptotic curves for the Fermi diad of ν_4 and $3\nu_6$ in ${}^{13}CH_3Cl$.

and $2[A'(1-\zeta) - B'] = 8.60 \text{ cm}^{-1}$, from which $\zeta_4 = +0.07_4$, using $A'' = 5.124 \text{ cm}^{-1}$ as found by Jones *et al.*, for ¹²CH₃Cl (2). The unperturbed band center of ν_4 is best found by assuming the ${}^{R}Q_{R}$ branches to be unperturbed and analyzing them in terms of the constants derived above and Eq. (2). [Since W is small in a resonance such as this (see below), at any distance from the point of resonance $(\nu_4 - \nu_{666})/2 \gg W$ in Eq. (1) and W can be neglected.] In this way, we find the band center for unperturbed ν_4 to be located at $3030.4_2 \pm 0.15 \text{ cm}^{-1}$. For the band

 $3\nu_6$, we make use of data derived later from the analysis of the fundamental, ν_6 . From this, we find for $3\nu_6$ that $[(A' - A'') - (B' - B'')] = +0.063 \text{ cm}^{-1}$ and $\zeta_{\text{eff}} = \zeta_6 = +0.241$. Further, it is a property of Eq. (1) that

$$(\nu^+ - \nu_4) = (\nu_{666} - \nu^-)$$

for any value of m. For m = 0, it is found that $(\nu^+ - {}^{R}Q_0)_{\nu_4} = +0.04 \text{ cm}^{-1}$, so we may assume that ${}^{R}Q_0$ for unperturbed $3\nu_6$ occurs at 3026.1 cm⁻¹, and the band center of $3\nu_6$ is located at 3023.6 cm⁻¹.

The curves for the unperturbed Q branches of the bands ν_4 and $3\nu_6$, calculated according to the equations

$$P_{, R}Q_{K}(\nu_{4}) = 3034.4 + 8.60m - 0.025m^{2},$$

 $P_{, R}Q_{K}(\nu_{666}) = 3026.1 + 7.01m + 0.063m^{2},$

are reproduced in Fig. 2, and will be seen to fit the experimental points very well, the observed weak ${}^{R}Q_{\kappa}$ branches of the lower component being accurately predicted by the curve for $3\nu_{6}$.

The point of resonance occurs almost exactly at ${}^{P}Q_{4}$ in the two bands. At this point, $\nu_{4} = \nu_{666}$ in Eq. (1), where these frequencies are given by the above equations with m = -4, and so we have the relation

$$\nu^+ - \nu^- = 2W,$$

from which we calculate the Fermi resonance interaction constant $W = 4.0 \pm 0.5$ cm⁻¹.

The corresponding band, ν_4 , in ¹²CH₃Cl exhibits the same characteristics of the intensity alternation becoming out of step, Q branch broadening and erratic Q branch separations near the band center. As a result, difficulty has been experienced in numbering the Q branches, and recent estimates for the band center vary (1, 2). A re-analysis of this band in terms of Fermi resonance between ν_4 and $3\nu_6$ is performed at the end of this paper.

$$(II) \ \nu_5 \ , \ 1450 \ cm^{-1}$$

This band is very similar in appearance to the corresponding band in ¹²CH₃Cl, which is depicted in Fig. 4 of Ref. 2. The three-fold intensity alternation of the Q branches is evident in the band, but ${}^{R}Q_{0}$ is abnormally weak and is split into at least three components. The Q branches are observed to degrade to higher wave numbers, the degree of degradation becoming much more marked as they approach the parallel fundamental, ν_{2} , at 1342 cm⁻¹, both of which effects are strong evidence of a significant Coriolis interaction taking place between ν_{2} and ν_{5} . Such a Coriolis interaction between a parallel and a perpendicular band in a symmetric top molecule affects the J structure in each of the bands, and will have the effect of altering the apparent B value for the upper state in each of the

| K' | <i>K</i> ″ | Q branch maxima | K' | K'' | Q branch maxima |
|----|------------|-----------------|----|----------|-----------------|
| 13 | 12 | 1594.01 | 3 | 2 | 1480.98 |
| 12 | 11 | 1583.20 | 2 | 1 | 1469.03 |
| 11 | 10 | 1572.76 | 1 | 0 | 1456.69 |
| 10 | 9 | 1561.20 | 0 | 1 | 1445.00 |
| 9 | 8 | 1550.07 | 1 | 2 | 1432.96 |
| 8 | 7 | 1538.88 | 2 | 3 | 1421.11 |
| 7 | 6 | 1527.64 | 3 | 4 | 1408.73 |
| 6 | 5 | 1515.46 | 4 | 5 | 1396.09 |
| 5 | 4 | 1504.60 | 5 | 6 | 1383.66 |
| 4 | 3 | 1492.91 | | | |

| TABLE V | | | | | | | |
|------------------|-------------|----|-----|---------------------------------------|---------|-------------|--|
| Branch | FREQUENCIES | OF | THE | ${}^{13}\mathrm{CH}{}_{3}\mathrm{Cl}$ | ν_5 | FUNDAMENTAL | |
| (con-1 in again) | | | | | | | |

K sub-bands. The visual effect of this will be most apparent in the Q branches of the sub-bands in the perpendicular band as the point of resonance is approached.

Although the effects of the rotational J structure associated with each subband was discernible in the spectrum, no analysis was possible. Some evidence of the effect of the restriction $J \ge K$ on the rotation lines was observed and so the numbering of the Q branches could be determined unequivocally. The lack of fine structure in the rotation lines was almost certainly due to the effect of the overlapping spectrum of ¹²CH₃Cl in the sample, which was compensated in the reference beam. Accordingly, we have no means of determining the sub-band origins. Measurements were made of the Q branch maxima and these are tabulated in Table V. The values were used in the conventional combination sum and difference relations obtained from the equation for the Q branch origins in a perpendicular band

$$P_{P,R}Q_{K} = \nu_{0} + [A'(1-\zeta)^{2} - B'] \pm 2[A'(1-\zeta) - B']K + [(A' - A'') - (B' - B'')]K^{2},$$

and graphical analysis yielded the results

$$\nu_{0} + [A'(1 - \zeta_{5})^{2} - B'] = 1457.21 \pm 0.15 \text{ cm}^{-1},$$

$$[(A' - A'') - (B' - B'')] = -0.046 \pm 0.006 \text{ cm}^{-1},$$

$$\zeta_{5} = -0.263 \pm 0.005,$$

$$\nu_{0} = 1449.54 \pm 0.15 \text{ cm}^{-1}.$$

The two latter results were obtained using $B'' = 0.42684 \text{ cm}^{-1}$ (3) and $A'' = 5.124 \text{ cm}^{-1}$ (2). Jones *et al.* found for α_5^B (¹²CH₃Cl) a value of -0.0007 cm⁻¹

Q

| K' | K'' | Q branch maxima | J_{\max} | Q branch origins |
|----------|-----|-----------------|------------|------------------|
| 11 | 10 | 1085.91 | 20 | 1085.24 |
| 10 | 9 | 1078.64 | 19 | 1078.03 |
| 9 | 8 | 1071.39 | 18.5 | 1070.81 |
| 8 | 7 | 1064.22 | 18 | 1063.67 |
| 7 | 6 | 1056.87 | 17 | 1056.38 |
| 6 | 5 | 1049.69 | 16.5 | 1049.23 |
| 5 | 4 | 1042.60 | 16 | 1042.16 |
| 4 . | 3 | 1035.45 | 15.5 | 1035.06 |
| 3 | 2 | 1028.32 | 15.5 | 1027.91 |
| 2 | 1 | 1021.33 | 15 | 1020.95 |
| 1 | 0 | 1014.36 | 15 | 1013.98 |
| 0 | 1 | 1007.44 | 15 | 1007.06 |
| 1 | 2 | 1000.50 | 15 | 1000.12 |
| 2 | 3 | 993.60 | 15.5 | 993.19 |
| 3 | 4 | 986.86 | 15.5 | 986.45 |
| 4 | 5 | 980.14 | 16 | 979.71 |
| 5 | 6 | 973.49 | 16.5 | 973.04 |
| 6 | 7 | 966.90 | 17.5 | 966.37 |
| 7 | 8 | 960.33 | 18 | 959.79 |
| 8 | 9 | 953.69 | 19 | 953.08 |

TABLE VI Q BRANCH FREQUENCIES OF THE ¹³CH₃Cl ν_6 FUNDAMENTAL (CM⁻¹ in vacuo)

(2). There is no reason to believe that α_5^{B} (¹³CH₃Cl) should be significantly different, so we may derive further for ν_5 of ¹³CH₃Cl

 $\alpha_5^{\ B} = -0.001 \text{ cm}^{-1}; \qquad \alpha_5^{\ A} = +0.047 \pm 0.01 \text{ cm}^{-1}.$

In the analysis of the ν_5 perpendicular bands of ${}^{12}\text{CH}_3\text{Cl}$ and ${}^{13}\text{CH}_3\text{Cl}$ in the conventional manner, it must be realised that the perturbations to the line frequencies caused by the Coriolis interactions with ν_2 are in each case being accounted for in terms of the rotational constants derived. Since α_5^B is apparently very small, the error in calculating the band center, ν_0 , from Q branch maxima instead of Q branch origins should be very small.

(III) ν_6 , 1011 cm⁻¹

This band exhibits a very regular Q branch structure, all branches degrading noticeably to lower wave numbers. No rotational fine structure was measurable, but the K numbering of the Q branches was rendered easy by the regular contour of the band as a whole, ${}^{R}Q_{0}$ being the most intense Q branch. The Q branch maxima from ${}^{R}Q_{10}$ to ${}^{P}Q_{9}$ were measured and the values are tabulated in Table VI. Since the microwave value of α_{6}^{B} is known for ${}^{12}\text{CH}_{3}\text{Cl}$ (5), and we would expect the value for ${}^{13}\text{CH}_{3}\text{Cl}$ to be closely similar, the Q branch maxima were converted to Q branch origins, ν_{sub} , using the equation

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TABLE VII

| FUNDAMENTAL | VIBRATION | FREQUENCIES | AND | ROTATIONAL | Constants | FOR |
|--|-----------|-------------|-----|------------|-----------|-----|
| ¹³ CH ₃ Cl in cm ⁻¹ | | | | | | |

| Α″ | | | 5.124 | Ref. (2) |
|-----------------|------------------------|----------------|-----------------------------|--------------|
| \mathbf{B}'' | | | 0.42684 | Refs. (3, 5) |
| | | | (0.41996, ³⁷ Cl) | |
| ν_1 | 2964.38 | α_1^A | +0.058 | This work |
| | | $\alpha_1{}^B$ | ~ 0.000 | Ref. (2) |
| ν_2 | 1349.42 | α_2^A | $\approx \alpha_2^B$ | This much |
| | $(1349.09, {}^{37}Cl)$ | $\alpha_2{}^B$ | $+0.0038_{3}$ | 1 mis work |
| Vj | 714.885 | $\alpha_3{}^A$ | $\approx \alpha_3^B$ | |
| | $(708.98, {}^{37}C1)$ | $\alpha_3{}^B$ | +0.0037 | I his work |
| | | Š 4 | $+0.07_{4}$ | This second |
| ν_4 | 3030.42 | $\alpha_4{}^A$ | +0.025 | I IIIS WOLK |
| | | $\alpha_4{}^B$ | ~ 0.000 | Ref. (11) |
| | | 55 | -0.263 | This ment |
| ν _{.ö} | 1449.54 | $\alpha_5{}^A$ | +0.047 | 1 ms work |
| | | $\alpha_5{}^B$ | ~ -0.001 | Ref. (2) |
| | | ζõ | +0.241 | This work |
| ν_6 | 1011.42 | α_6^A | -0.019 | THIS WOLK |
| | | $\alpha_6{}^B$ | +0.0016 | Ref. (5) |
| | | | | |

(ZETA CONSTANTS DIMENSIONLESS)

$$P_{R}^{P, R}Q_{K}(J_{\max}) = Q_{\max} = \nu_{\text{sub}} + (B' - B'')J_{\max}(J_{\max} + 1)$$

where J_{max} is the value of J corresponding to the most intense line in the Q branch. This may readily be found from the equation for the rotation line intensities

$$I \alpha (2J+1) A_{KJ} e^{-F(K,J)hc/kT},$$

where the A_{KJ} are the Hönl–London rotational intensity factors (10). The values for J_{max} derived from the ground state rotational constants for ¹³CH₃Cl and the resulting Q branch origins using $\alpha_6^B = +0.0016 \text{ cm}^{-1}$ are tabulated in Table VI alongside the corresponding Q branch maxima. The calculated Q branch origins are in close agreement with our visual estimates in the band. Graphical analysis of the Q branch origins in the conventional manner, assuming $A'' = 5.124 \text{ cm}^{-1}$ and $B'' = 0.42684 \text{ cm}^{-1}$, lead to the results

$$\begin{split} \nu_0 + [A'(1 - \zeta_6)^2 - B'] &= 1013.96 \pm 0.03 \text{ cm}^{-1}, \\ [(A' - A'') - (B' - B'')] &= +0.0206 \pm 0.0006 \text{ cm}^{-1}, \\ \zeta_6 &= +0.241 \pm 0.003, \\ \nu_0 &= 1011.42 \pm 0.03 \text{ cm}^{-1}, \\ \alpha_6^{-B} &= +0.0016 \text{ cm}^{-1} \text{ (assumed from microwave)}, \\ \alpha_6^{-A} &= -0.019 \pm 0.001 \text{ cm}^{-1}. \end{split}$$

C. TABULATION OF RESULTS

RE-ANALYSIS OF V4 BAND IN ¹²CH₃Cl in Terms of Fermi Resonance with 3V6

The overall appearance of this band is reproduced in Fig. 2 of Ref. 2, and the Q branch maxima frequencies reported there are used in this analysis. (Our estimates were almost identical.) As reported in Ref. 2, near the expected band center the Q branch spacing becomes abnormally small and the three-fold intensity alternation is upset. The authors observe this to be due to a marked localized perturbation and obtain values for [(A' - A'') - (B' - B'')] and ζ_4 from the asymptotes of a graph of Q branch spacing against K. However, their numbering for the lower component of the diad is incorrect by 3 units, and the effect of the localized resonance in terms of the renumbered Q branches is shown in Fig. 3. The graph of Q branch spacing against m (m = +K for the ^RQ branches and = -K for the ^PQ branches) is asymptotic to the theoretical straight line plot for the Q branch spacings of unperturbed ν_4 , from which we find

$$[(A' - A'') - (B' - B'')] = -0.025 \text{ cm}^{-1}$$

and $2[A'(1 - \zeta_4) - B'] = 8.598 \text{ cm}^{-1}$, giving $\zeta_4 = +0.07_1$. The value for $\alpha_4^A - \alpha_4^B$ is in excellent agreement with the value found for the parallel component of $2\nu_4$ by Brown and Edwards (11). The band center of unperturbed ν_4 was obtained by assuming the high ${}^{R}Q_{R}$ branches to be essentially unperturbed and back-calculating for ${}^{R}Q_0$ in terms of the molecular constants derived above. In this way, we find $\nu_0 = 3041.6 \pm 0.3 \text{ cm}^{-1}$. The curve representing unperturbed ν_4 was best given by the expression

$$P_{R}^{P_{R}}Q_{K}(\nu_{4}) = 3045.5 + 8.598m - 0.025m^{2},$$

and this curve is drawn in Fig. 3 in relation to the measured Q branch positions.

For $3\nu_6$, we find from the fundamental, ν_6 , $[(A' - A'') - (B' - B'')] = +0.069 \text{ cm}^{-1}$ and $\zeta_{\text{eff}} = \zeta_6 = +0.238$. Estimating unperturbed ${}^{R}Q_0$ as before from the relation $(\nu^+ - {}^{R}Q_0)_{\nu_4} = ({}^{R}Q_0 - \nu^-)_{\nu_{666}} = 1.3 \text{ cm}^{-1}$, the band center is located at 3038.7 cm⁻¹, and the curve representing unperturbed $3\nu_6$ is best given by the equation

$$P_{\mu} Q_{\kappa}(\nu_{666}) = 3041.3 + 7.034m + 0.069m^{2}$$

This curve is also drawn in Fig. 3. In contrast to the corresponding diad in ¹³CH₃Cl, no convincing evidence of any ${}^{R}Q_{\pi}$ branches of the lower component can be found in our spectra. This can be explained with reference to Fig. 3, where it will be seen that the ${}^{R}Q_{\pi}$ branches of the lower component, which will lie essentially on the unperturbed $3\nu_{6}$ curve, will occur at almost exactly the same frequency as the much stronger ${}^{R}Q_{\kappa-1}$ series of the main ν_{4} band.



FIG. 3. The observed Q branch positions (\odot) and the asymptotic curves for the Ferm diad of ν_4 and $3\nu_6$ in ${}^{12}CH_3Cl$.

The unperturbed band centers of ν_4 and $3\nu_6$ lie very close in this case, the separation being only $\sim 3 \text{ cm}^{-1}$. From Fig. 3, the exact point of resonance will be seen to occur close to ${}^{P}Q_2$ in the two bands, and at this point, as before,

$$\nu^+ - \nu^- = 2W,$$

from which we estimate the Fermi resonance interaction constant, $W = 4.0 \pm 0.5$ cm⁻¹, the same value as that found for the interaction in the corresponding band in ¹³CH₃Cl. In this case, the effects of the resonance interaction are more marked

since the two band centers are almost exactly degenerate and so it is in the region of the band center of ν_4 that the perturbation is most evident.

Note added in proof. Since this paper was written, the results of two independent analyses of the Fermi diad, $\nu_4/3\nu_6^2$, in ${}^{12}\text{CH}_3\text{Cl}$ have come to the attention of the authors. The first, by C. Bétrencourt-Stirnemann, C. Joffrin-Graffouillère, M. Morillon-Chapey, and C. Alamichel, *Comptes rendus*, **264B**, 1458 (1967), was performed under conditions of higher resolution than that reported in this paper. The second (A. G. Maki and R. Thibault, to be published) has been performed under conditions of very high resolution, and therefore should yield the most precise results. Considering that the point of maximum resonance is very close to the two band centers, which render the latter most sensitive to any uncertainties in the analyses, the three sets of results are in very good agreement.

| | This work | B-S et al. | M and T |
|---|---------------|--------------|-------------|
| ν4 | 3041.6 | ∽3040.29 | 3039.25 |
| 54 | $+0.07_{1}$ | +0.06 | $+0.06_{0}$ |
| $(\alpha^A - \alpha^B)_{\nu_A}$ | +0.025 | +0.026 | +0.026 |
| $3\nu_6^1$ | 3038.7 | not quoted | 3042.82 |
| $(\zeta_{\rm eff})_{3\nu_6}^{1}$ | +0.238(ass.) | +0.235 | $+0.23_{2}$ |
| $(\alpha^A - \alpha^B)_{3\gamma_6}^{1}$ | -0.069(ass.) | +0.026(ass.) | -0.086 |
| W | 4.0 ± 0.5 | 3.9 | 3.519 |
| | | | |

The authors would like to thank Drs. Maki and Thibault for sending them a copy of their paper prior to publication.

ACKNOWLEDGMENTS

The authors are grateful to the Science Research Council and the Royal Society for research grants which enabled the purchase of the spectrometer and additional recording apparatus. A. A. is grateful to the Science Research Council for a Research Studentship, during the tenure of which this work was carried out. The authors would like also to express their thanks to Dr. D. C. McKean who suggested this study.

RECEIVED: July 8, 1967

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