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A first study of the ν_6 fundamental of CF_2Cl_2

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Résumé. — Nous avons effectué l'étude spectroscopique de la molécule $CF_2{}^{35}Cl_2$ dans la région de 923 cm^{-1} avec, d'une part, un spectre de laser à diode donnant la branche Q de la bande ν_6 et, d'autre part, un spectre par transformée de Fourier de 910 à 935 cm^{-1}. La superposition des nombreuses bandes d'absorption dans cette région donne une grande densité de raies non isolées qui rend leur identification très difficile même à la résolution du laser à diode (0,001 5 cm^{-1}).
Nous avons, à partir de la branche Q, déterminé des constantes rotationnelles qui permettent de reproduire les raies jusqu'à $J = 78$. A l'aide de ces constantes, nous avons calculé la branche R et le spectre calculé est en bon accord avec le spectre par transformée de Fourier enregistré avec une résolution de 0,04 cm^{-1}.

Abstract. — The spectral region near 923 cm^{-1} is studied by using diode laser spectra of the dominant Q-branch belonging to the $CF_2{}^{35}Cl_2$ molecule along with Fourier transform spectra of the entire region from 910 to 935 cm^{-1}. The overlap of the many absorption bands and also the large density of lines make quantum identification difficult because even at the resolving power of the diode laser (0.001 5 cm^{-1}) the lines observed are not pure. However, rotational constants have been found which reconstruct the Q-branch lines up to $J = 78$. The profile of the R-branch calculated from these constants is in fair agreement with the Fourier transform spectra from 925 to 935 cm^{-1} recorded at a resolution of 0.04 cm^{-1}.

1. **Introduction.** — Interest in CF_2Cl_2, along with other halogen-containing molecules arose when it was suspected that these molecules might play an important role in the chemistry of stratospheric ozone [1]. The spectral features of CF_2Cl_2, commonly called fluorocarbon-12, have been observed in balloon-borne [2] and ground-based [3, 4] high resolution infrared atmospheric measurements which use the sun as a source. The successes of these *in situ* programs to model the concentration and distribution of atmospheric CF_2Cl_2 depend on a precise knowledge of the energy levels and transition frequencies of the molecule.

The strong, narrow Q-branch features of CF_2Cl_2 near 923 cm^{-1} prove to be ideal for atmospheric detection of even small concentrations as seen in figure 4 of reference [3] and on a more recent solar spectrum recorded at a resolution of 0.04 cm^{-1} with a Nicolet interferometer at The Ohio State University. The strong absorption features in the spectrum are caused by atmospheric water-vapour, and make observation of the entire band profile of CF_2Cl_2 impossible. Nevertheless, the Q-branch features are visible in the spectrum. Spectra recorded by balloon-borne instruments of the same resolving-power show much less water-vapour absorption, and the entire band of CF_2Cl_2 in this region is clearly visible [2]. Quantitative high resolution spectral analysis of this band of CF_2Cl_2 has not been made up to this point.

2. **General remarks.** — The CF_2Cl_2 molecule has an almost tetrahedral structure with the carbon atom at the centre as shown in figure 1. This asymmetric-top molecule belongs to the point group C_{2v} when both chlorine atoms are the same isotopic variety. As seen in the figure, the AB-symmetry plane is the plane of the Cl-C-Cl bond, and the BC-symmetry plane is the plane of the F-C-F bond. The point G represents the centre of mass of the molecule. If the two chlorine atoms are different isotopes, only the AB-plane

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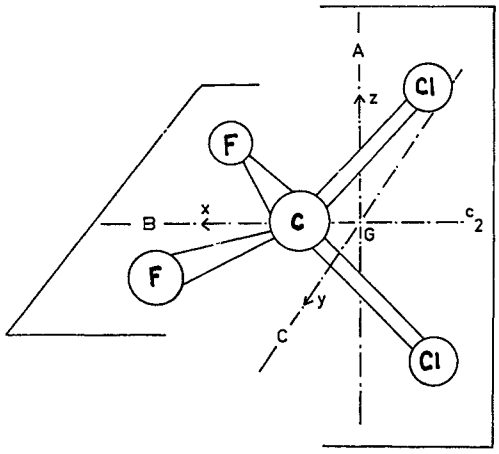

Fig. 1. — Geometry of CF_2Cl_2 molecule. *A*, *B* and *C* axes are indicated such that $I_A < I_B < I_C$.

remains a symmetry plane and the molecule then belongs to the C_s point group.

It is important at this point to discuss the isotopic varieties of this molecule, since they complicate the spectrum near 923 cm^{-1}. Chlorine-35 and chlorine-37 exist in an abundance ratio of approximately 3 : 1. Thus, $CF_2{}^{35}Cl_2$, $CF_2{}^{35}Cl^{37}Cl$, $CF_2{}^{37}Cl_2$ exist in a ratio of approximately 9 : 6 : 1. In the region near 923 cm^{-1}, absorption bands of all three isotopic varieties are visible in the spectrum. No bands in the 923 cm^{-1} region have so far been attributed to the carbon-13 isotope. In the work presented here, only the dominant isotopic variety $^{12}CF_2{}^{35}Cl_2$ has been studied. However, before the 923 cm^{-1} region is well understood, it will be necessary to study all of the possible isotopic species.

3. **Ground state.** — The microwave spectrum of the vibrational ground state of CF_2Cl_2 has been studied by Takeo and Matsumura [5] and by Su and Beeson [6]. Rotational constants and centrifugal distortion constants for the ground state are given in reference [5] and we have converted their distortion constants to the values given in table I. However, it was found that the standard deviation for each constant was of the order of the value of the constant.

Table I. — *Rotation and distortion constants for the ground state of the* ^{35}Cl-^{35}Cl *isotope of* CF_2Cl_2.

Constants	Takeo and Matsumura (*)	This work (see text)
A	0.137 399 3 (13) cm^{-1}	0.137 398 5 (5) cm^{-1}
B	0.088 022 4 (7)	0.088 021 5 (5)
C	0.074 513 0 (7)	0.074 512 0 (5)
Δ_J	4.436 08 E-8	1.427 80 E-8 (**)
Δ_{JK}	− 1.164 3 E-8	− 9.403 35 E-9 (**)
Δ_K	5.504 1 E-8	5.042 47 E-8 (**)
δ_J	3.715 E-9	3.113 E-9 (**)
δ_K	0.0 (fixed)	4.589 1 E-9 (**)

(*) Converted from constants given in : Harutoshi Takeo and Chi Matsumura, *Bull. Chem. Soc. Japan* **50** (1977) 636.

(**) Fixed to the value suggested by Mills.

For this reason, microwave transition frequencies and assignments given in references [5] and [6], were used in a least-squares calculation, and a very good fit with the data was found (± 0.32 MHz) using only rotation constants *A*, *B* and *C*, with the distortion constants fixed to zero. It is for this reason that the distortion constants are difficult to evaluate. Further least-squares fits were tried in which each distortion constant was liberated separately. The results of this program showed that only the inclusion of Δ_K improved the fit, but that the improvement was only slight.

Mills [7] has provided us with a set of distortion constants for the ground state of CF_2Cl_2. These constants were derived from force field calculations based on known force fields of CF_4 and CCl_4. With the distortion constants fixed to the theoretical values suggested by Mills, a final least-squares calculation was performed to the microwave data [5, 6] to determine the rotational constants. Table I also lists the distortion constants along with the accompanying rotational constants obtained in this way. Although the differences between Takeo and Matsumura's values and the values obtained from the calculations of Mills are not large, it was decided to adopt the latter set of constants to represent the ground state. The value of the asymmetry constant κ is − 0.57.

4. **Spectrum analysis.** — The infrared spectrum of CF_2Cl_2 along with other halogenated-methanes has been studied under low resolution by Plyler and Benedict [8]. The symmetry species of the vibrational levels adopted here agree with the assignments for CF_2Cl_2 given in their paper. The band at 922 cm^{-1} is identified as an asymmetric stretching of the carbon-chlorine bonds. This fundamental is assigned the name ν_6 and the symmetry of the vibrational level is B_1 in this scheme. The change of the dipole moment of the molecule is along the *A*-axis, and therefore the ν_6 band is a type-a band.

A closer look at the region near 923 cm^{-1} is provided in figure 2. This spectrum was recorded at The Ohio State University on a Nicolet interferometer. The nominal resolution in this spectrum is 0.04 cm^{-1}. Two interpretations of the spectral features seen here have been proposed, the first by Goldman *et al.* [9] and the second more recently by Giorgianni *et al.* [10]. These last authors have different labelling for vibra-

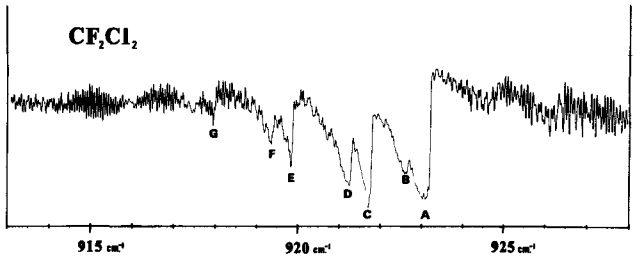

Fig. 2. — Spectrum at 0.04 cm^{-1} resolution of ν_6 band of CF_2Cl_2 which shows, the overlap of many bands.

Table II. — *Interpretations of Q-branches in the spectral region near* 923 cm^{-1}.

Q-Branch position in figure 3	Approximate frequency	Goldman [9]	Giorgianni [10]
—	—	—	—
A	923.1 cm^{-1}	v_6 (Cl : 35-35)	v_6 (Cl : 35-35)
B	922.6	$v_4 + v_6 - v_4$	$v_5 + v_6 - v_5$ (Cl : 35-35)
C	921.8	v_6 (Cl : 35-37)	$v_4 + v_6 - v_4$ (Cl : 35-35)
D	921.3	$v_5 + v_6 - v_6$	v_6 (Cl : 35-37)
E	919.9	v_6 (Cl : 37-37)	$v_4 + v_6 - v_4$ (Cl : 35-37)
F	919.4	—	v_6 (Cl : 37-37)
G	918.0	—	$v_4 + v_6 - v_4$ (Cl : 37-37)

tions; nevertheless, a conversion of their notation can be made and their results compared in table II.

This second interpretation seems to be better because it explains all the Q-branch features seen in figure 2, and the three Q-branch of the v_6 fundamentals are equidistant. With this interpretation given by Giorgianni the distance between the ^{35}Cl-^{35}Cl fundamental and the ^{37}Cl-^{37}Cl fundamental is approximately 3.7 cm^{-1}. The harmonic force field calculations in reference [10] predict a spacing of only 2.5 cm^{-1}. This discrepancy can be explained by the existence of a Fermi resonance between the v_6 (B_1) and the combination band v_3 (A_1) + v_7 (B_1) for each isotope. According to the harmonic force field calculation, the computed isotopic shift in the combination band is approximately 13.7 cm^{-1}, with ^{35}Cl-^{35}Cl : $v_3 + v_7$ = 904.2 cm^{-1} and ^{37}Cl-^{37}Cl : $v_3 + v_7$ = 890.5 cm^{-1}. Thus, the ^{35}Cl-^{35}Cl bands of v_6 and $v_3 + v_7$ fall closer together than the same bands of ^{37}Cl-^{37}Cl in the absence of resonance. With resonance present, the resonance splits the levels of the ^{35}Cl-^{35}Cl isotopic molecule more than the levels of the ^{37}Cl-^{37}Cl isotopic molecule. The result is that the v_6 fundamentals for the two isotopic varieties of CF_2Cl_2 are pushed farther apart than the expected 2.5 cm^{-1}.

High resolution diode laser spectra in a few narrow spectral regions have been recorded by one of us [11] at NASA/Goddard Space Flight Centre. Figure 3

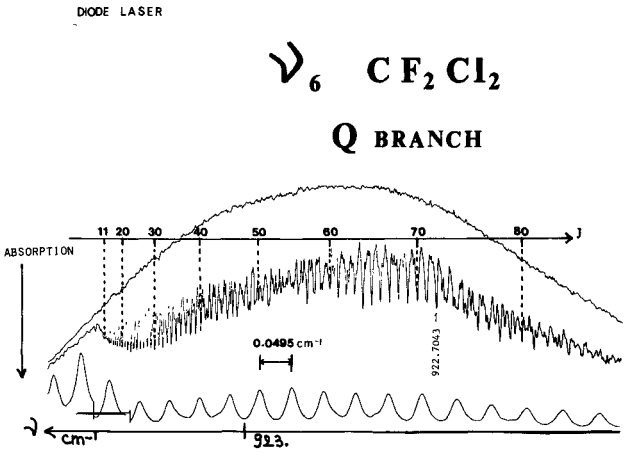

Fig. 3. — High resolution diode laser spectrum of Q-branch region for v_6 of $CF_2{}^{35}Cl_2$.

shows the region of the strongest Q-branch where the line width is approximately 0.001 5 cm^{-1}. The frequency positions of many of these absorption lines were measured directly using ammonia frequency standards and the germanium etalon fringe spacing of 0.049 5 cm^{-1}.

Analysis of the diode laser spectrum has proceeded from the assumption that the structure seen in the spectrum is caused by an increase in the J quantum number within the main Q-branch. A group of thirty well-defined absorption lines above 923 cm^{-1} was fitted to an equation of the form

$$\nu = b_0 + b_1 J(J+1) + b_2 J^2(J+1)^2 \qquad (1)$$

using different J values for the start of the series. The best fit was found when the first absorption line visible near the band origin was assigned the value $J = 11$. By extrapolation, a few J values above 40 were assigned to absorption lines in the spectrum near 923 cm^{-1} until the observed frequency and calculated frequency differed by more than 0.002 cm^{-1}. A new least-squares fit was made which included the new J assignments, and with this fit a few more J values were assigned by extrapolation. In this way, J values up to $J = 78$ were assigned to absorption lines in the spectrum. J values between 57 and 78 fell on the series of strong absorption lines visible in the spectrum below 923 cm^{-1}. A final least-squares fit was made using all the J values between 11 and 78.

Absorption lines of the same J but different K were assumed to fall together at the same frequency. This assumption was based on the fact that the absorption lines appear to be symmetric, showing no K-structure to high or low frequencies, and also on the fact that the J-structure by itself explains all the lines. This preliminary assignment and hypothesis for the interpretation of the Q-branch spectrum was used as input for an asymmetric-top, least-squares program which determined the rotational and distortion constants for the $v_6 = 1$ energy level. For the present reconstruction Δ'_{JK}, Δ'_K, δ'_J and δ'_K of the v_6 level were fixed to the ground state values. Table III lists the constants for the v_6 fundamental which were derived from the fit to the Q-branch spectrum.

The observed minus calculated values for all of the

Table III. — *Rotation and distortion constants for the* $v_6 = 1$ *level of the* ^{35}Cl-^{35}Cl *isotope of* CF_2Cl_2.

Constants	$v_6 = 1$
v_0	923.245 8 cm^{-1}
A	0.137 291 8 cm^{-1}
B	0.087 914 8
C	0.074 405 3
Δ_J	1.357 5 E-8 (*)
Δ_{JK}	− 9.403 35 E-9 (*)
Δ_K	5.042 47 E-8 (*)
δ_J	3.113 E-9 (*)
δ_K	4.589 1 E-9 (*)

(*) Fixed to the ground state values in table I. Quoted uncertainties are standard deviations of least squares calculation.

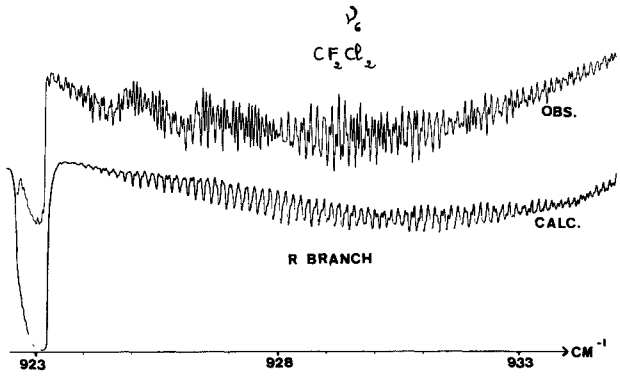

Fig. 4. — R-branch reconstruction using constants generated from the Q-branch spectrum.

absorption lines were within ± 0.002 cm^{-1}, and most were within ± 0.001 cm^{-1}.

Using these constants, an asymmetric-top program was used to reconstruct the Q-branch spectrum. The intensities of the observed absorption lines are well reproduced, and this reconstruction shows that the most intense Q-branch lines occur for $K_a = J$.

These constants were then used to reconstruct the P- and R-branches. The P-branch for the ^{35}Cl-^{35}Cl isotope is obscured by the many overlapping bands discussed earlier. The reconstruction of the R-branch is shown in figure 4 : the extent of the band is well reproduced.

Before better agreement can be made between observed R-branch lines and calculated lines, it will be necessary to observe spectra of cooled samples of fluorocarbon-12, and to obtain spectra of isotopically enriched samples. Only then can the problem of overlapping bands in this spectral region be solved. Furthermore, resonances between the v_6 fundamental and other absorption bands will most certainly have to be included before a better picture of the entire v_6 absorption band can be made.

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