September, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2505—2511 (1979) 2505

Measurement and Analysis of the ν_3 Band of CF_4

Tetsuo Suzuki, Hiroshi Okada, and Tsunetake Fujiyama*

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

(Received March 2, 1979)

The ν_3 fundamental of carbon tetrafluoride has been measured with a tunable diode laser-source spectrometer. The following molecular constants were obtained: $\nu_0-2(B\zeta_3)_{\rm eff}=1283.4067$ cm^{-1}, $B^{\rm PR}_{\rm eff}+B_0-2(B\zeta_3)_{\rm eff}=7.210\times10^{-2}$ cm^{-1}, $B^{\rm PR}_{\rm eff}-B_0=-5.290\times10^{-4}$ cm^{-1}, and $\delta_3=6.153\times10^{-4}$ cm^{-1}. Using the r_g-structure obtained from the gas-electron diffraction study, the above molecular constants were reduced to be: $\nu_0=1283.7181$ cm^{-1}, $B^{\rm PR}_{\rm eff}=0.1915$ cm^{-1}, $B_0=0.1920$ cm^{-1}, and $(B\zeta_3)_{\rm eff}=0.1557$ cm^{-1}. From the $(B\zeta_3)_{\rm eff}$ value, the Coriolis coupling constant for the ν_3 was estimated to be $\zeta_3=0.811$.

Although carbon tetrafluoride is one of the most simple and basic molecules belonging to the point group T_d, very few studies of its rotation-vibration spectra have been reported. This has been largely due to the deficiency in the resolving power of the spectrometers. Edgell *et al.* have observed the ν_3 and ν_4 fundamentals with a rather low-resolution spectrometer and estimated the Coriolis coupling constants, ζ_3 and ζ_4, by analyzing the band contours.1) The rotation-vibration spectra have been observed for the ν_4 fundamental by Maki *et al.* with a resolution of 0.06 cm^{-1}. From the *J*-structure analysis, the molecular constants, ν_0, $B(1-\zeta_4)$, and B_4-B_0, were determined.2) The ν_4 fundamental of three isotope species, ^{12}C, ^{13}C, and ^{14}C, were observed with a resolution of 0.06 cm^{-1} by Jones *et al.*3) The observed spectra were well resolved into *J*-structures, and the molecular constants for the three isotope species were determined.

In the case of the ν_3 fundamental, however, the spacing of the rotational structure is so narrow that the conventional spectrometer cannot resolve its fine structures. The present report will concern itself with the measurement of the rotation-vibration spectra for the ν_3 fundamental of carbon tetrafluoride by the use of a tunable diode laser-source spectrometer and with the analysis of the rotation-vibration spectra.

Experimental

The sample used in this study was a commercial product and was used without further purification. The survey spectrum of the ν_3 band of carbon tetrafluoride was recorded from 1270 to 1290 cm^{-1} using a Nicolet 7199 Fourier transform infrared spectrometer at a 0.06-cm^{-1} resolution. The observation was made at room temperature using a 10-cm gas cell. The sample pressure was about 0.5 Torr.

The high-resolution spectrum was recorded from 1281.28 to 1282.92 cm^{-1} by the use of a tunable diode laser-source spectrometer, (Laser Analytics model LS series). The observation was made at room temperature using a 15-cm gas cell. The pressure was 0.1—0.2 Torr. The resolution of the instrument was 10^{-4}—10^{-3} cm^{-1}; therefore, the line width of the observed spectrum was governed by the Doppler broadening. The line frequencies were calibrated by the use of the (100-000) and (11^10-01^10) transition frequencies of the N_2O vapor4,5) and the interference fringes arising from a germanium etalon whose free spectral range was 0.04841 cm^{-1} at 1282 cm^{-1}. The precision of the frequency measurement was believed to be 0.002 cm^{-1}, while the accuracy of the frequency measurement was restricted by the ambiguity to be expected in the determination of the band origin of the standard lines. It was, however, believed to be better than 0.005 cm^{-1}.4,5)

Observed Spectra

The spectra of the ν_3 band recorded by the Fourier transform spectrometer is shown in Fig. 1. There appear an R branch centered around 1285—1286 cm^{-1}, a strong Q branch at 1283 cm^{-1}, and a broad P branch. Overlapped with the P branch, there appear a relatively strong absorption maximum at 1281 cm^{-1} and a weak absorption maximum at 1279 cm^{-1}. Probably the two absorption maxima arise from hot bands. As is shown in Fig. 1, the P and R branches are resolved into fine structures. However, these fine structures cannot easily be identified as *J*-components because their intensities and spacings do not show any apparent regularities.

The intensities of the Q branch at 1283 cm^{-1} and the Q branch of the hot band at 1281 cm^{-1} were carefully measured at various sample pressures. The observed intensity ratio was 1 : 0.231. As the intensity ratio of the Q branch of the ν_3 fundamental and that of the $\nu_3+\nu_2-\nu_2$ hot band is 1 : 0.238, the relatively strong absorption maximum observed at 1281 cm^{-1} is identified as the Q branch of the $\nu_3+\nu_2-\nu_2$ hot band.

The high-resolution spectrum observed by the use of the diode laser-source spectrometer is shown in Fig. 2. In the region from 1281.80 to 1282.72 cm^{-1}, a series of *J*-components of the P branch can be seen clearly, and each *J*-component is further resolved into sub-structure components. The spectrum in the 1282.72—1282.92 cm^{-1} region is quite complex because it is overlapped with the strong Q branch. As the frequency decreases, the spacing of the sub-structure components becomes larger relative to the spacing of the *J*-components. Therefore, it becomes difficult to identify a *J*-component as a definite line group.

It seems that most of the sub-structure components are not completely resolved, because their line-widths are much broader than the Doppler width. The Doppler width is estimated to be about 0.002 cm^{-1} under these experimental conditions.

Analysis of the Observed Band

Rotational Energy Levels of the Ground and Excited Vibrational States. The present analysis is based on the theoretical work reported by Herranz.6)

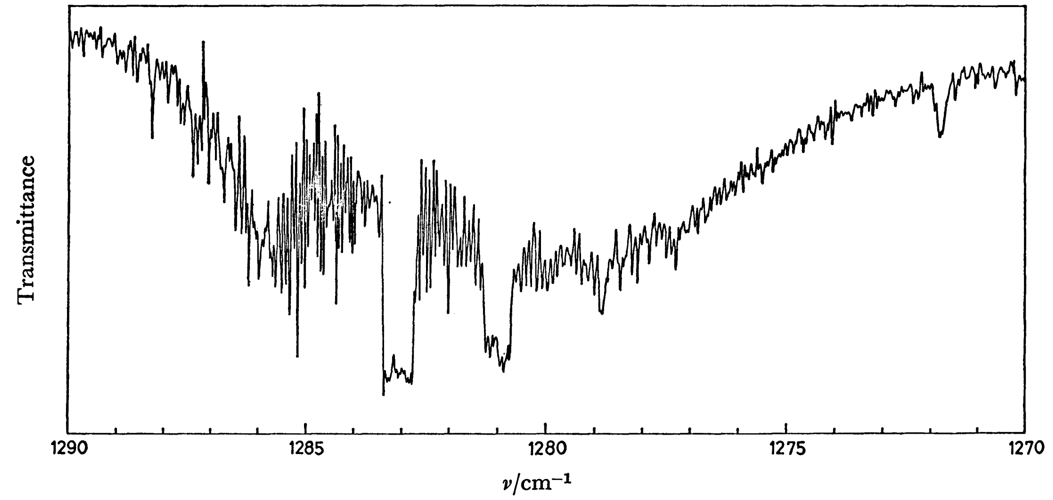

Fig. 1. The spectrum of the ν_3 band recorded by the Fourier transform spectrometer.

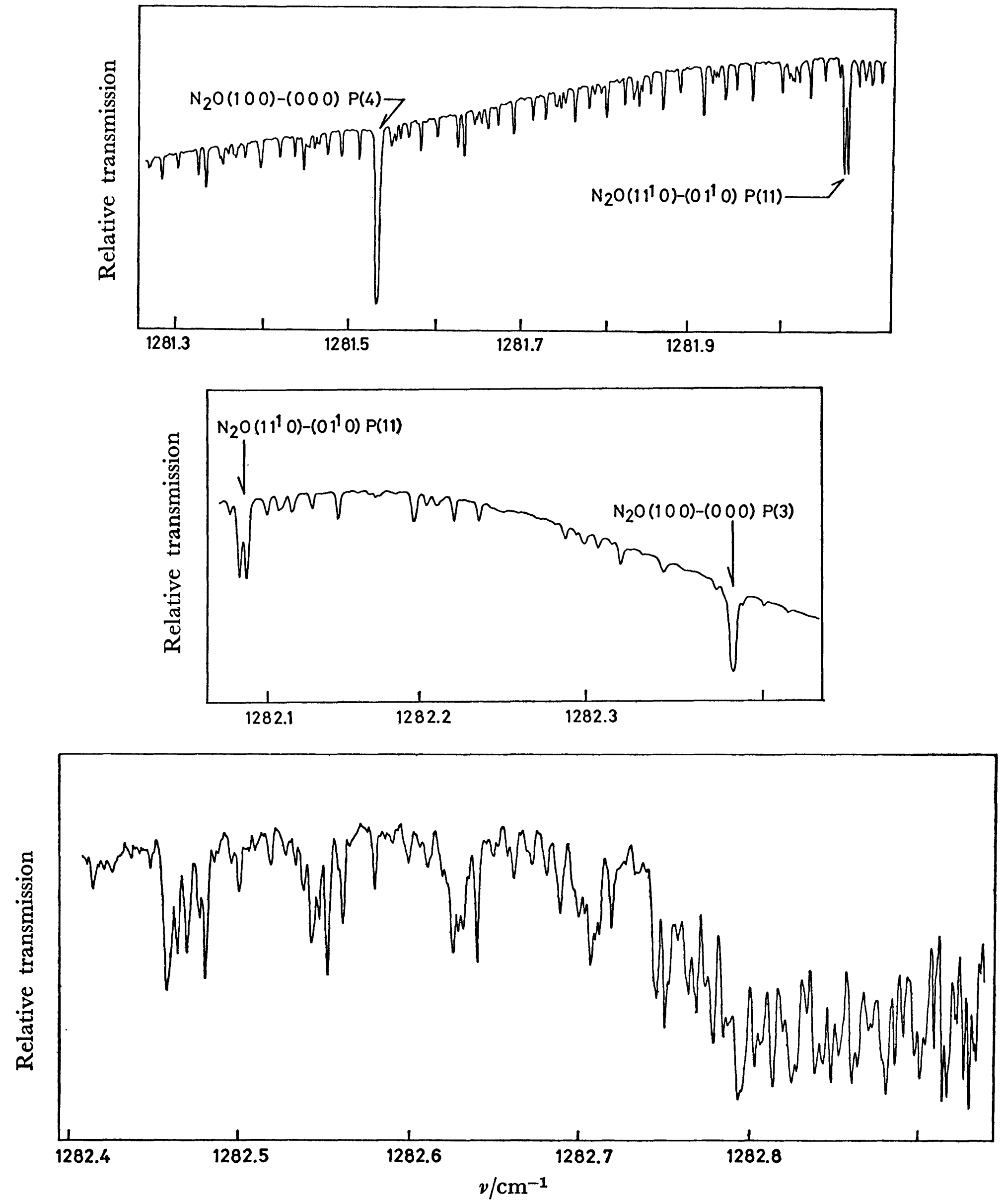

Fig. 2. The high resolution spectrum of the ν_3 band observed by the use of the tunable diode laser source spectrometer.

The term values for the rotational levels of the ground state of an XY_4-type spherical-top molecule can be written as:

$$F_0(J,\tau) = B_0J(J+1) - D_0^JJ^2(J+1)^2 - D^{J\tau}S_{J,\tau}, \qquad (1)$$

where B_0 and $D_0{}^J$ are the rotational constant and the centrifugal distortion constant for the ground state respectively. The last term of Eq. 1 represents the splitting of the rotational levels into their sublevels as a consequence of centrifugal distortion. There are $2J+1$ sublevels for each J value including degeneracy; these sublevels are designated by an index, τ. $S_{J,\tau}$ is the eigenvalue of the angular momentum operator:

$$S = P_x^4 + P_y^4 + P_z^4 - (3/5)P^4 + (1/5)P^2, \qquad (2)$$

where:

$$P^2 = P_x^2 + P_y^2 + P_z^2, \text{ and } P^4 = (P_x^2+P_y^2+P_z^2)^2.$$

When the wavefunctions of an axially symmetric rotor are chosen as a basis set, the nonvanishing matrix elements for S are:

$$\begin{aligned}(J,K|S|J,K) &= (3/20)(J^2+J)(J^2+J-2-10K^2)\\ &\quad + (1/4)K^2(7K^2+5) \qquad (3a)\end{aligned}$$

and:

$$\begin{aligned}(J,K|S|J,K\pm4) &= (1/8)\{(J\mp K)(J\mp K-1)\\ &\quad\times(J\mp K-2)(J\mp K-3)(J\pm K+1)\\ &\quad\times(J\pm K+2)(J\pm K+3)(J\pm K+4)\}^{1/2} \qquad (3b)\end{aligned}$$

when the triply degenerate vibrational mode is excited, the interaction of rotation and vibration removes the degeneracy; therefore, each J level splits into three levels. They are designated by (+), (0), and (−). Each of these levels is further split into sublevels. These sublevels are designated by the same index, τ, as in the ground state. For each J value the number of sublevels is $2J+3$ for the (+), $2J+1$ for the (0), and $2J-1$ for the (−) levels.

The term values for the rotational levels of the excited vibrational state are given by:

$$\begin{aligned}F^{(+)}(J,\tau) &= B_{\text{eff}}^{\text{PR}}J(J+1) + 2(B\zeta_3)_{\text{eff}}J - D_1^JJ^2(J+1)^2\\ &\quad + \frac{S_{J+1,\tau}}{2J^2+3J+1}\{\delta_3 - D^{J\tau}(2J^2-5J+3)\} \qquad (4a)\\ F^{(0)}(J,\tau) &= B_{\text{eff}}^{\text{Q}}J(J+1) - 2(B\zeta_3)_{\text{eff}} - D_1^JJ^2(J+1)^2\\ &\quad - \frac{S_{J,\tau}}{J^2+J}\{\delta_3 + D^{J\tau}(J^2+J-10)\} \qquad (4b)\\ F^{(-)}(J,\tau) &= B_{\text{eff}}^{\text{PR}}J(J+1) - 2(B\zeta_3)_{\text{eff}}(J+1) - D_1^JJ^2(J+1)^2\\ &\quad + \frac{S_{J-1,\tau}}{2J^2+J}\{\delta_3 - D^{J\tau}(2J^2+9J+10)\} \qquad (4c)\end{aligned}$$

where $B_{\text{eff}}^{\text{PR}}$ is the effective rotational constant for the (+) and (−) levels, while $B_{\text{eff}}^{\text{Q}}$ is that for the (0) level. The δ_3 parameter represents the splitting of the J level resulting from the instantaneous breakdown of symmetry which is produced by the vibrational mode. The explicit expression for δ_3 is given in Ref. 6. In order to further specify the characteristics of the sublevels, the τ index is replaced by a double index, nT. The symbol T specifies the type of degeneracy of the sublevel; that is, $T=A$, $T=E$, and $T=F$ refer to nondegenerate, doubly degenerate, and triply degenerate sublevels respectively. The symbol n differentiates the sublevels belonging to the same J and T; that is, $n=1$ refers to the sublevel of the largest $S_{J,\tau}$, $n=2$ refers to the sublevel of the second largest $S_{J,\tau}$, and so on.

The selection rules for electric dipole transitions are:

$$\begin{aligned}\Delta\tau = 0 \text{ and } \Delta J &= -1 \quad \text{for } F^{(+)}\leftrightarrow F_0\\ \Delta J &= 0 \quad \text{for } F^{(0)}\leftrightarrow F_0\\ \Delta J &= 1 \quad \text{for } F^{(-)}\leftrightarrow F_0.\end{aligned}$$

Taking account of these selection rules, the line frequencies of the fundamental band are expressed as: for the P branch:

$$\begin{aligned}\nu^{\text{P}}(J,\tau) &= \nu_0 - 2(B\zeta_3)_{\text{eff}} - \{B_{\text{eff}}^{\text{PR}}+B_0-2(B\zeta_3)_{\text{eff}}\}J\\ &\quad + \{(B_{\text{eff}}^{\text{PR}}-B_0)-(D_1^J-D_0^J)\}J^2 + 2(D_1^J+D_0^J)J^3\\ &\quad - (D_1^J-D_0^J)J^4 + \frac{S_{J,\tau}}{2J^2-J}\{\delta_3+(8J-10)D^{J\tau}\}\end{aligned} \qquad (5a)$$

for the Q branch:

$$\begin{aligned}\nu^{\text{Q}}(J,\tau) &= \nu_0 - 2(B\zeta_3)_{\text{eff}} + (B_{\text{eff}}^{\text{Q}}-B_0)J(J+1)\\ &\quad - (D_1^J-D_0^J)J^2(J+1)^2 - \frac{S_{J,\tau}}{J^2+J}(\delta_3-10D^{J\tau})\end{aligned} \qquad (5b)$$

and for the R branch:

$$\begin{aligned}\nu^{\text{R}}(J,\tau) &= \nu_0 - 2(B\zeta_3)_{\text{eff}} + \{B_{\text{eff}}^{\text{PR}}+B_0-2(B\zeta_3)_{\text{eff}}\}(J+1)\\ &\quad + \{(B_{\text{eff}}^{\text{PR}}-B_0)-(D_1^J-D_0^J)\}(J+1)^2\\ &\quad - 2(D_1^J-D_0^J)(J+1)^3 - (D_1^J-D_0^J)(J+1)^4\\ &\quad + \frac{S_{J,\tau}}{2J^2+5J+3}\{\delta_3-(8J+18)D^{J\tau}\}. \qquad (5c)\end{aligned}$$

J takes the values 1, 2,⋯; 1, 2,⋯, and 0, 1, 2,⋯ for the P, Q, and R branches respectively.

The relative intensities of the lines are given by:

$$\begin{aligned}I_{\text{P}}(J,\tau) &= g_T(2J-1)\nu^{\text{P}}(J,\tau)\exp\left\{-\frac{hcF_0(J,\tau)}{kT}\right\}\\ &\quad\times\left[1-\exp\left\{-\frac{hc\nu^{\text{P}}(J,\tau)}{kT}\right\}\right]\\ I_{\text{Q}}(J,\tau) &= g_T(2J+1)\nu^{\text{Q}}(J,\tau)\exp\left\{-\frac{hcF_0(J,\tau)}{kT}\right\}\\ &\quad\times\left[1-\exp\left\{-\frac{hc\nu^{\text{Q}}(J,\tau)}{kT}\right\}\right]\\ I_{\text{R}}(J,\tau) &= g_T(2J+3)\nu^{\text{R}}(J,\tau)\exp\left\{-\frac{hcF_0(J,\tau)}{kT}\right\}\\ &\quad\times\left[1-\exp\left\{-\frac{hc\nu^{\text{R}}(J,\tau)}{kT}\right\}\right] \qquad (6)\end{aligned}$$

where g_T is the nuclear spin statistical weight factor; T, the temperature; h, the Planck constant; c, the light velocity, and k, the Boltzmann constant. As the spin value of a fluorine atom is 1/2, the g_T values are given by:

$$g_A = 5,\ g_E = 2, \text{ and } g_F = 3. \qquad (7)$$

Assignment. First our attention was focused on the high-resolution spectrum from 1282.00 to 1282.72 cm^{-1}, because a clear series of J-components appears. These lines certainly belong to a P-branch-line series of $J>7$. The definite assignment of each line can

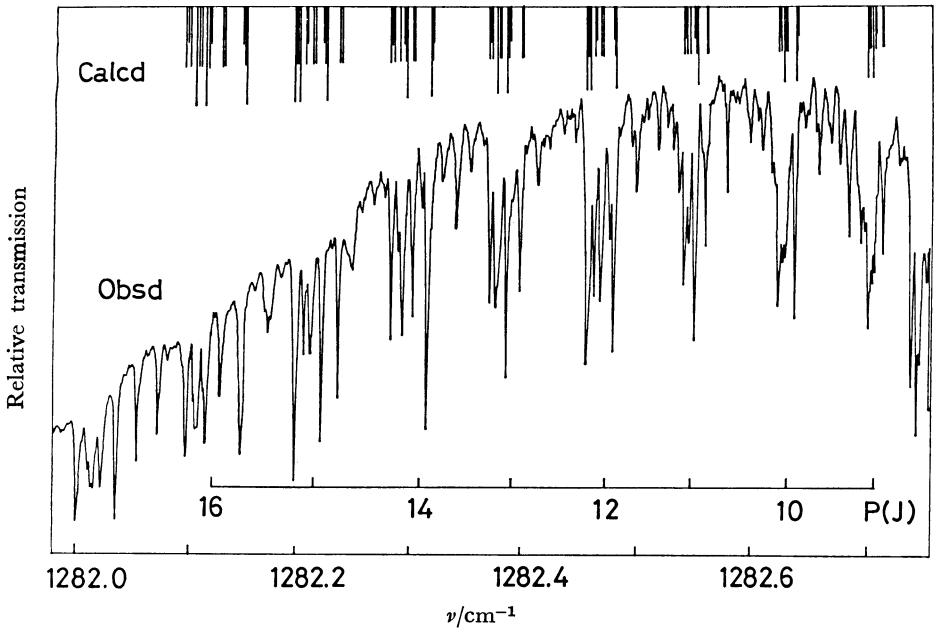

Fig. 3. The observed and calculated spectra in the frequency region of 1282.0—1282.7 cm^{-1}.

be made by calculating the theoretical relative intensities and the relative spacings of the sub-structure components. In Fig. 3, the spectrum calculated from Eqs. 5a, 6, and 7 is compared with the observed spectrum. It can be seen from the figure that some of the observed lines are not completely resolved into the sub-structure components. The Doppler width is sometimes larger than the spacing of the sub-structure components. It is not possible at present to resolve the spectrum of this band into the sub-structures completely by the use of an ordinary spectroscopic method. Therefore, we defined the hypothetical observed frequency for the unresolved lines as:

$$\nu_{\max} = \frac{\sum \nu(J,\tau)I(J,\tau)}{\sum I(J,\tau)}. \tag{8}$$

By doing so, the frequency at the intensity maximum of an unresolved line can be used as an observed frequency. The molecular constants, $\nu_0-2(B\zeta_3)_{\mathrm{eff}}$, $B_{\mathrm{eff}}^{\mathrm{PR}}+B_0-2(B\zeta_3)_{\mathrm{eff}}$, and δ_3 were tentatively determined from the P-branch lines of $9\leq J\leq 16$ by the least-squares method. Smaller weights were given for the lines which were not fully resolved. Then, the final assignment of all the observed lines from 1281.3 to 1282.72 cm^{-1} was made by the use of the approximate frequencies of the transition lines calculated from these tentatively determined molecular constants and the theoretical relative intensities. The P-branch lines of $J\leq 8$ cannot be found, because they are buried in the strong Q branch.

The observed spectral features of the Q branch were so complex that its analysis was abandoned.

Determination of the Molecular Constants. The molecular constants were determined from the P-branch lines of $9\leq J\leq 24$ by the least-squares method. The lines which were not fully resolved were given smaller weights. As the number of the observed lines is not enough, the following assumptions were made in the present analysis: $D_1^J=D_0^J$ and the value of D_0^J was fixed at 2.5×10^{-7} cm^{-1}, which has been obtained from the analysis of the ν_4 fundamental.[3] In addition, as the value of $D^{J\tau}$ is theoretically estimated to be 4×10^{-8} cm^{-1} by using the rotational constant[7] and the harmonic force field,[8] the effect of this constant can be regarded as negligible on analyzing the absorption lines of $J\leq 24$. Therefore, we put $D^{J\tau}=0$ in the least-squares fitting.[9]

The molecular constants which were obtained from the least-squares fitting are listed in Table 1. The observed and calculated frequencies are summarized in Table 2. The standard deviation of the fit is 0.0023 cm^{-1}. For the P(15) lines, the differences between the observed and calculated frequencies are about two times as large as those for the other lines; the reason for this is not yet clear.[10]

Table 1. The molecular constants obtained from ν_3 band of CF_4 (in cm^{-1})

$\nu_0-2(B\zeta_3)_{\mathrm{eff}}$	1283.4067 ± 0.0044
$B_{\mathrm{eff}}^{\mathrm{PR}}+B_0-2(B\zeta_3)_{\mathrm{eff}}$	$(7.210\pm 0.054)\times 10^{-2}$
$B_{\mathrm{eff}}^{\mathrm{PR}}-B_0$	$-(5.290\pm 0.160)\times 10^{-4}$
δ_3	$(6.153\pm 0.110)\times 10^{-4}$

The uncertainties are twice the standard deviations.

Discussion. The molecular constants, ν_0, $(B\zeta_3)_{\mathrm{eff}}$, $B_{\mathrm{eff}}^{\mathrm{PR}}$, and B_0, cannot be determined independently from the analysis of the P branch of the ν_3 band alone. However, these constants can be independently determined if we use the r_g-structure obtained from the gas-electron-diffraction study. The rotational constant in the ground state can be calculated following the idea of Morino *et al.*[11]

The nuclear-distance parameter, r_α, is expressed as:

$$r_\alpha = r_g - \frac{\{\langle(\Delta x)^2\rangle+\langle(\Delta y)^2\rangle\}}{2r_e} - \delta_r \tag{9}$$

where $\langle(\Delta x)^2\rangle$ and $\langle(\Delta y)^2\rangle$ are the mean-square

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES OF ν_3 BAND

Assignment		Observed frequency (cm^{-1})	Calculated frequency (cm^{-1})	$\Delta^{a)}$ (cm^{-1})
J	τ			
P(9)	1F, 2F	1282.7195	1282.7230	0.0035
	1E, 3F	1282.7123	1282.7153	0.0030
	1A	1282.7098	1282.7127	0.0029
	4F, 5F, 2A	1282.7074	1282.7095	0.0021
P(10)	1E, 1F, 1A	1282.6412	1282.6431	0.0019
	2F, 3F	1282.6327	1282.6339	0.0012
	2A	1282.6298	1282.6305	0.0007
	4F, 2E, 5F	1282.6266	1282.6269	0.0003
P(11)	1F, 2F	1282.5615	1282.5625	0.0010
	1A, 3F, 1E	1282.5526	1282.5524	−0.0002
	4F	1282.5476	1282.5472	−0.0004
	5F, 2E, 6F	1282.5430	1282.5425	−0.0005
P(12)	1A, 1F, 1E	1282.4811	1282.4812	0.0001
	2F, 3F	1282.4705	1282.4695	−0.0010
	2E, 4F	1282.4648	1282.4630	−0.0018
	2A, 5F, 6F, 3A	1282.4584	1282.4570	−0.0014
P(13)	1F, 2F	1282.3992	1282.3991	−0.0001
	1E, 3F, 1A	1282.3870	1282.3859	−0.0011
	4F, 5F, 2A	1282.3773	1282.3768	−0.0005
	6F, 2E, 7F	1282.3722	1282.3702	−0.0020
P(14)	1A, 1F, 1E	1282.3167	1282.3162	−0.0005
	2F, 3F	1282.3033	1282.3021	−0.0012
	2A, 4F, 2E	1282.2958	1282.2934	−0.0024
	5F	1282.2912	1282.2886	−0.0026
	6F, 2E, 7F	1282.2848	1282.2823	−0.0025
P(15)	1F, 2F	1282.2371	1282.2328	−0.0043
	1A, 3F, 1E	1282.2236	1282.2175	−0.0061
	4F, 5F	1282.2133	1282.2069	−0.0064
	2E, 6F	1282.2075	1282.2011	−0.0064
	2A, 7F, 8F, 3A	1282.1998	1282.1935	−0.0063
P(16)	1A, 1F, 1E	1282.1507	1282.1485	−0.0022
	2F, 3F	1282.1340	1282.1318	−0.0022
	2E, 4F	1282.1233	1282.1205	−0.0028
	2A	1282.1215	1282.1187	−0.0028
	5F, 6F	1282.1151	1282.1128	−0.0023
	3A	1282.1126	1282.1103	−0.0023
	7F, 3E, 8F	1282.1052	1282.1033	−0.0019
P(17)	1F, 2F	1282.0639	1282.0635	−0.0004
	1E, 3F, 1A	1282.0462	1282.0455	−0.0007
	4F, 5F	1282.0335	1282.0328	−0.0007
	2A	1282.0272	1282.0265	−0.0007
	6F, 2E	1282.0245	1282.0237	−0.0008
	7F	1282.0213	1282.0204	−0.0009
	8F, 3E, 9F	1282.0122	1282.0120	−0.0002
P(18)	1E, 1F, 1A	1281.9764	1281.9778	0.0014
	2F, 3F	1281.9569	1281.9586	0.0017
	2A, 4F, 2E	1282.9433	1281.9449	0.0016
	5F	1282.9347	1281.9364	0.0017
	6F	1282.9320	1281.9334	0.0014
	3E, 7F	1282.9279	1281.9294	0.0015
	3A, 8F, 9F, 4A	1282.9180	1281.9197	0.0017
P(19)	1F, 2F	1281.8890	1281.8914	0.0024
	1A, 3F, 1E	1281.8686	1281.8711	0.0025
	4F, 5F	1281.8536	1281.8558	0.0022
	2E, 6F	1281.8436	1281.8457	0.0021
	2A	1281.8405	1281.8424	0.0019
	7F	1281.8359	1281.8386	0.0027
	8F, 3A	1281.8341	1281.8362	0.0021
	9F, 3E, 10F	1281.8237	1281.8262	0.0025
P(20)	1A, 1F, 1E	1281.8019	1281.8043	0.0024
	2F, 3F	1281.7811	1281.7827	0.0016
	2E, 4F, 2A	1281.7639	1281.7661	0.0022
	5F, 6F	1281.7525	1281.7545	0.0020
	3A	1281.7467	1281.7493	0.0026
	7F, 3E	1281.7426	1281.7452	0.0026
	8F	1281.7399	1281.7424	0.0025
	9F, 4E, 10F	1281.7294	1281.7316	0.0022
P(21)	1F, 2F	1281.7149	1281.7165	0.0016
	1E, 3F, 1A	1281.6923	1281.6937	0.0014
	4E, 5F	1281.6741	1281.6760	0.0019
	2A, 6F, 2E	1281.6624	1281.6636	0.0012
	7F	1281.6542	1281.6560	0.0018
	8F	1281.6492	1281.6514	0.0022
	3E, 9F	1281.6460	1281.6482	0.0022
	3A, 10F, 11F, 4A	1281.6329	1281.6360	0.0031
P(22)	1E, 1F, 1A	1281.6261	1281.6280	0.0019
	2F, 3F	1281.6025	1281.6039	0.0014
	2A, 4F, 2E	1281.5840	1281.5851	0.0011
	5F, 6F	1281.5717	1281.5709	−0.0008
	3E, 7F	1281.5608	1281.5618	0.0010
	3A	1281.5554	1281.5565	0.0011
	8F	1281.5527	1281.5538	0.0011
	9F, 4A	1281.5500	1281.5516	0.0016
	10F	b)		
	4E	b)		
	11F	b)		
P(23)	1F	b)		
	2F	b)		
	1A, 3F, 1E	1281.5137	1281.5136	−0.0001
	4F, 5F	1281.4938	1281.4935	−0.0003
	2E, 6F, 2A	1281.4779	1281.4777	−0.0002
	7F	1281.4684	1281.4682	−0.0002
	8F	1281.4666	1281.4663	−0.0003
	3A	1281.4629	1281.4628	−0.0001
	9F, 3E	1281.4575	1281.4571	−0.0004
	10F	1281.4552	1281.4548	−0.0004
	11F, 4E, 12F	1281.4412	1281.4413	0.0001
P(24)	1A, 1F, 1E	1281.4516	1281.4490	−0.0026
	2F, 3F	1281.4249	1281.4225	−0.0024
	2E, 4F, 2A	1281.4040	1281.4011	−0.0029
	5F, 6F	1281.3877	1281.3846	−0.0031
	3A	1281.3777	1281.3745	−0.0032
	7F, 3E	1281.3755	1281.3721	−0.0034
	8F	1281.3691	1281.3662	−0.0029
	9F	c)		
	4E, 10F	1281.3605	1281.3572	−0.0033
	4A, 11F, 12F, 5A	1281.3456	1281.3423	−0.0033

a) Δ = (calculated frequency) − (observed frequency). b) Not observed because of overlapping with N_2O lines. c) Not observed because of overlapping with other lines.

amplitudes of the harmonic vibrations perpendicular to the internuclear axis, r_g is the internuclear distance which is directly observed by the gas-electron-diffraction method, and δ_r is the small correction for the centrifugal distortion. On the other hand, a moment of inertia in the ground state, I_{zero}, is expressed as:

$$I_{\text{zero}} = I_0\left(1-\sum_{s}\frac{g_s}{2B_0}\alpha^{\text{harm.}}\right) \tag{10}$$

where I_0 is effective moment of inertia obtained from spectroscopy, $\alpha^{\text{harm.}}$, the harmonic part of the vibration-rotation constant, and g_s, the degree of vibrational degeneracy. The relation between the nuclear-distance parameter, r_z, which is derived from I_{zero}, and the nuclear distance parameter, r_α, of Eq. 9 is:

$$\lim_{T\to 0} r_\alpha \equiv r^0 = r_z. \tag{11}$$

Therefore, r_α can be regarded as r_z if the normal frequencies are much larger than kT/hc. In the case of carbon tetrafluoride, therefore, we get:

$$r_z(\text{C–F}) = (1.3172\pm 0.0004)\times 10^{-8}\,\text{cm}, \quad \text{and}$$

$$B_0 = 0.1920\pm 0.0001\,\text{cm}^{-1},$$

using $r_g(\text{C–F}) = (1.3197+0.0004)\times 10^{-8}$ cm, which was determined by Fink *et al.*,[7] and the harmonic force field of Ref. 8. The values of the molecular constants which were calculated from the B_0 value and the molecular constants of Table 1 are summarized in Table 3.

TABLE 3. THE MOLECULAR CONSTANTS (in cm^{-1}) DETERMINED BY USING THE r_g-STRUCTURE AND THE PRESENT RESULTS

ν_0	1283.7181 ± 0.0044
$B_{\text{eff}}^{\text{PR}}$	0.1915 ± 0.0001
B_0	0.1920 ± 0.0001
$(B\zeta_3)_{\text{eff}}$	0.1557 ± 0.0003

It is of some interest to estimate the Coriolis coupling constant from the observed $(B\zeta_3)_{\text{eff}}$ value. $(B\zeta_3)_{\text{eff}}$ is written as:[6)]

$$(B\zeta_3)_{\text{eff}} = B_e\zeta_3 + (3/4)\beta_3 \tag{12}$$

where;

$$\beta_3 = (1/3)(B_{\text{eff}}^{\text{Q}} - B_{\text{eff}}^{\text{PR}}). \tag{13}$$

From these equations, ζ_3 is given by:

$$\zeta_3 = \frac{(B\zeta_3)_{\text{eff}} - (1/4)(B_{\text{eff}}^{\text{Q}} - B_{\text{eff}}^{\text{PR}})}{B_e}. \tag{14}$$

In order to determine the ζ_3 value, the as-yet-undetermined $B_{\text{eff}}^{\text{Q}}$ and B_e values are necessary. If we assume that these relations hold:

$$|B_{\text{eff}}^{\text{Q}} - B_{\text{eff}}^{\text{PR}}| \lesssim |B_{\text{eff}}^{\text{PR}} - B_0|$$

and:

$$|B_0 - B_e| \lesssim |B_{\text{eff}}^{\text{PR}} - B_0|,$$

then ζ_3 is approximately expressed as:

$$\zeta_3 \simeq (B\zeta_3)_{\text{eff}}/B_0. \tag{15}$$

The error expected in the ζ_3 value thus calculated is of the order of $(2|B_{\text{eff}}^{\text{PR}} - B_0|)/B_0$. Thus, we obtained $\zeta_3 = 0.811\pm 0.006$. Edgell *et al.* determined the Coriolis conpling constant for the ν_3 band, $\zeta_3 = 0.84$, by an analysis of the P-R-branch separation of the ν_3 envelope.[1)] The present result is significantly smaller than their result. The Coriolis coupling constant for the ν_4 band was obtained by Jones *et al.*[3)] Their result, $\zeta_4 = -0.366$, predicts that the ζ_3 value will be about 0.866, because of the Corilois sum rule, $\zeta_3 + \zeta_4 = 0.5$. The present estimation is much smaller than their prediction. The reason for this disagreement is not yet clear and must be left for future study.

Incidentally, we wish to add a few lines on a future problem in high-resolution spectroscopy using a tunable diode laser-source spectrometer. In this study, detailed molecular constants could not be obtained, although the spectra have been recorded by the use of a tunable diode laser-source spectrometer whose instrumental resolution was 10^{-4}—10^{-3} cm^{-1}. The reason for this are thought to be:

1) The precision and accuracy of the frequency measurement is not satisfactory enough, although the instrumental resolution surprisingly high.

2) It is difficult to tune a diode laser in the required frequency region and over a wide frequency range.

3) Since an observed linewidth is governed by the Doppler broadening, an effective spectral resolution is not essentially improved very much.

The authors wish to express their thanks to Dr. Shigeo Kondou, of the National Chemical Laboratory for Industry, for obtaining the spectrum recorded by the Fourier transform spectrometer. The authors also would like to thank professor Eizi Hirota, of the Institute for Molecular Science, for giving them the opportunity to use the tunable diode laser-source spectrometer.

References

1) W. F. Edgell and R. E. Moynihan, *J. Chem. Phys.*, **27**, 155 (1957).

2) A. Maki, E. K. Plyler, and R. Thibault, *J. Chem. Phys.*, **37**, 1899 (1962).

3) L. H. Jones, B. J. Krohn, and W. C. Kennedy, *J. Mol. Spectrosc.*, **70**, 288 (1978).

4) R. P. Grosso and T. K. McCubbin, Jr., *J. Mol. Spectrosc.*, **13**, 240 (1964).

5) J. Dupre-Maquaire and P. Pinson, *J. Mol. Spectrosc.*, **58**, 239 (1975).

6) J. Herranz, *J. Mol. Spectrosc.*, **6**, 343 (1961).

7) M. Fink, C. W. Schmiedekamp, and D. Gregory, *J. Chem. Phys.*, to be published.

8) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, *J. Mol. Spectrosc.*, **19**, 78 (1966).

9) We tried to determine the molecular constants, including the centrifugal distortion constants, with the assumption that $D_0^J = D_1^J$. The following molecular constants were obtained by the least-squares method:

$$\nu_0 - 2(B\zeta_3)_{\text{eff}} = 1283.2978\pm 0.0092\,\text{cm}^{-1}$$

$$B_{\text{eff}}^{\text{PR}} + B_0 - 2(B\zeta_3)_{\text{eff}} = (5.050\pm 0.178)\times 10^{-2}\,\text{cm}^{-1}$$

$$B_{\text{dff}}^{\text{PR}} - B_0 = -(1.876\pm 0.110)\times 10^{-4}\,\text{cm}^{-1}$$

$D_0^J = (6.93\pm0.56)\times10^{-6}\,\mathrm{cm}^{-1}$

$\delta_3 = (6.123\pm0.054)\times10^{-4}\,\mathrm{cm}^{-1}$

However, these results seem to be unreasonable. The transition frequency of the R-branch line which is calculated from these molecular constants takes a maximum value at J=11 and then decreases $J>11$ as the J value increases. This is not consistent with the observed band profile of the R branch (see Fig. 1).

10) Even if we give zero weight to the P(15) lines in the least-squares fitting, the resultant molecular constants are very close to those in Table 1.

11) Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962).