The Microwave Spectra of Sulfur Tetrafluoride in the Excited Vibrational States. The Vibrational Assignment for ν_4 and ν_9

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The vibrational satellites of SF_4 have been observed for the two lowest bending modes, ν_4 and ν_9. The relative intensities which were observed are consistent with the vibrational assignment of Frey *et al.* but are incompatible with Levin's assignment. Consideration of the Coriolis interaction between the two modes lead to the same conclusion. The centrifugal distortion constants are evaluated and are compared with the observed.

In 1970 Christie and Sawodny[1] revised the previous assignments for the vibrational modes of sulfur tetrafluoride, by observing the Raman spectra in the gaseous state. Shortly after Frey *et al.*[2] proposed an assignment in which they reversed the two antisymmetric stretching bands, ν_6 and ν_8, based upon comparison with the vibrational spectra of the related molecules. Christie *et al.*[3] recently arrived at the same conclusion by evaluating the force constants. On the other hand Levin[4] observed two bands at 245 cm^{-1} and 206 cm^{-1} in the Raman spectrum of solid SF_4, which he ascribed to the two lowest bending modes, ν_4 and ν_9. Berney[5] has, however, shown that the band at 206 cm^{-1} is due to randomly-oriented oligomers. Christie *et al.*[3] also critisized the assignment of Levin by comparing the calculated mean amplitudes with the observed.

The rotational spectra in the excited states may provide us with information on the vibrational assignment, particularly in cases where two modes in near resonance are coupled by the Coriolis interaction[6]. If the ν_4 and ν_9 vibrations are nearly degenerate in the gas phase as argued by Levin, the rotational spectra in the two excited states would exhibit the effects of the Coriolis resonance, provided that the coupling constant is large enough. In the present work we observed the rotational spectra of SF_4 in the excited states of the ν_4 and ν_9 modes and obtained results which are consistent with the vibtational assignment of Frey *et al.*

Experimental

A sample of sulfur tetrafluoride was obtained by a method described in Inorganic Syntheses.[7] It is known that SF_4 reacts easily with water to form SOF_2. Our sample contains about 5—10% of SOF_2. Fortunately the microwave spectra of SOF_2 have recently been investigated in detail,[8] and thus we could identify easily the lines of SOF_2 in our observed spectra. Sulfur tetrafluoride decomposes quite rapidly in a glass vessel, and hence we stored the sample in a stainless steel holder equipped with a needle valve. Sulfur tetrafluoride was found quite stable in a Stark cell; we did not observe any appreciable decrease in intensity for two hours. We observed the microwave spectra of SF_4 at room temperature using a microwave spectrometer with a 120 kHz square-wave oscillator as a Stark modulator.

Rotational Spectra

The intensities of the ν_4 satellites relative to those of the ground state are the same for all types of the transitions, whereas those of the ν_9 satellites are dependent upon the parity of the K_{+1} number because of the two pairs of the equivalent fluorine nuclei. Table 1 lists the relative intensities which are calculated at T=300 K for the two vibrational assignments. It is to be noted that Levin assigned the bands at 228 cm^{-1} and at 233 cm^{-1} to ν_4 and ν_9 (or ν_9 and ν_4) in the gas phase, respectively.

TABLE 1. RELATIVE INTENSITIES OF THE ν_4 AND ν_9 SATELLITES OF SF_4 AT 300 K[a)]

Vibration	Transition	Frey *et al.*	Levin
ν_4 (A_1)	ee—oe, oo—eo	0.320	0.320
ν_9 (B_2)	ee—oe	0.103	0.187
	oo—eo	0.285	0.520

a) Relative to the ground-state transition.

Because several low-J R-branch transitions of $J=2\leftarrow 1$ and $J=3\leftarrow 2$ show characteristic Stark patterns, we first concentrated to search the vibrational satellites around the corresponding ground-state transitions, which were reported by Tolles and Gwinn[9]. Aside from the Stark patterns we also utilized the following relation among the three R-branch frequencies:

$$4\nu(3_{22}\leftarrow 2_{12}) = 3[\nu(2_{21}\leftarrow 1_{11}) + \nu(2_{11}\leftarrow 1_{01})].$$

Since the centrifugal distortion effects are very small for SF_4 as shown below, this relation holds accurately. In Fig. 1 we plotted $\nu(2_{11}\leftarrow 1_{01})/2$, $\nu(3_{22}\leftarrow 2_{12})/3$, and $\nu(2_{21}\leftarrow 1_{11})/2$ in equidistance. We adjusted the abscissa slightly so that the three ground-state lines are in line.

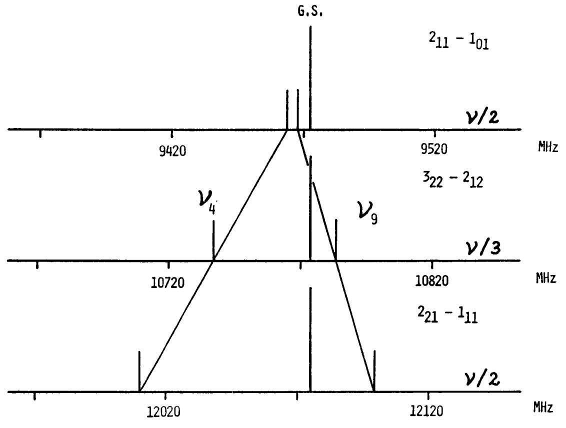

Fig. 1. Plot of the three R-branch frequencies, $\nu(2_{11}\leftarrow 1_{01})/2$, $\nu(3_{22}\leftarrow 2_{12})/3$, and $\nu(2_{21}\leftarrow 1_{11})/2$.

TABLE 2. OBSERVED FREQUENCIES OF SF_4 IN THE ν_4 AND ν_9 STATES (MHz)

Transition	ν_4 Obsd	ν_4 Δ[a)]	ν_9 Obsd	ν_9 Δ[a)]
2_{11}–1_{01}	18 929.188	0.082	18 935.565	0.076
2_{20}–1_{10}	23 331.027	−0.053	23 518.939	−0.053
2_{21}–1_{11}	24 020.927	0.049	24 199.162	−0.023
2_{20}–2_{12}	10 476.062	−0.012		
3_{12}–2_{02}	27 617.464	−0.060	27 568.640	−0.004
3_{21}–2_{11}	30 474.066	0.014	30 620.687	0.053
3_{22}–2_{12}	32 212.423	−0.015	32 350.800	−0.049
3_{30}–3_{22}	15 070.894	−0.011	15 429.284	−0.040
3_{31}–3_{21}	14 136.150	−0.039	14 562.058	0.071
3_{21}–3_{13}			12 701.624	−0.008
4_{31}–4_{23}	15 695.438	−0.033	16 002.389	0.081
4_{32}–4_{22}	13 065.330	0.019		
4_{40}–4_{32}	20 636.163	0.072		
5_{32}–5_{24}	17 057.299	−0.054		
5_{33}–5_{23}	11 443.225	−0.071		
5_{42}–5_{32}	19 938.522	0.002		
5_{50}–5_{42}	26 489.208	−0.065		
5_{41}–5_{33}			21 178.940	−0.086
6_{06}–5_{14}	27 574.120	0.107		
6_{25}–5_{33}	26 652.792	−0.102		
6_{34}–6_{24}	9 409.653	−0.056		
6_{43}–6_{33}	18 901.345	0.013		
6_{52}–6_{42}	26 223.992	−0.032		
6_{51}–6_{43}			27 060.470	0.015
7_{52}–7_{44}	26 232.490	0.096	26 929.460	0.010
8_{35}–8_{27}	28 913.758	0.193		
8_{53}–8_{45}	26 203.110	0.063		
9_{45}–9_{37}	26 075.965	−0.096		
9_{54}–9_{46}	26 460.532	0.105		
9_{64}–9_{54}	31 527.507	0.052		
10_{46}–10_{38}	30 489.551	−0.109		
10_{55}–10_{47}	27 302.000	0.028	27 713.130	−0.002
10_{64}–10_{56}	31 613.132	−0.283		
11_{56}–11_{48}	29 126.547	−0.077		
11_{65}–11_{57}	31 539.739	0.037		
11_{66}–11_{56}	29 480.457	0.068		
12_{66}–12_{58}	31 822.525	0.078		
13_{67}–13_{59}	32 788.690	0.038		
15_{79}–15_{69}	31 377.473	0.031		
$16_{7,10}$–$16_{6,10}$	27 945.594	−0.078		
$19_{8,12}$–$19_{7,12}$	31 166.284	0.019		

a) Obsd − Calcd The calculated frequencies are obtained using the constants listed in Table 3.

TABLE 3. ROTATIONAL CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF SF_4 IN THE ν_4 AND ν_9 STATES (MHz)[a)]

Constants	ν_4	ν_9
A	6641.7081 (84)	6707.7928 (71)
B	4095.8118 (89)	4075.9354 (94)
C	3213.7530 (90)	3217.9307 (93)
τ_{aaaa}	−0.01052 (76)	−0.0225 (19)
τ_{bbbb}	−0.00464 (63)	−0.0138 (19)
τ_{cccc}	−0.00136 (66)	0.0044 (43)
T_1[b)]	−0.0085 (11)	−0.0178 (33)
T_2[b)]	−0.00024 (84)	−0.0111 (27)

a) Values in parentheses denote the standard deviations and apply to the last significant digits. b) $T_1=\tau_{aabb}'+[(A-B)/(A-C)]\tau_{ccaa}'$ and $T_2=\tau_{bbcc}'+[(B-C)/(A-C)]\cdot\tau_{ccaa}'$.

Two sets of the vibrational satellites indicated in Fig. 1 obviously satisfy the above equation. Table 2 summarizes the observed frequencies of the two sets of the spectra. The rotational constants listed in Table 3 were determined by a least-squares analysis, where the centrifugal distortion effects were taken into account to the first order. The τ constants are not well determined as shown in Table 3.

Vibrational Assignment

The relative intensities of the two sets of the observed spectra are in good agreement with those given in Table 1 for the vibrational assignment of Frey *et al.* Further evidence which supports this conclusion is obtained by analyzing the Coriolis interaction.

The two modes under consideration couple with each other by the Coriolis interaction associated with the a-axis. Levin[4)] gave the force constants of valence-force type, which reproduce the vibrational frequencies corresponding to the two assignments. These force constants result in the Coriolis coupling constants $\zeta_{4,9}^{(a)}$ which are listed in Table 4.

TABLE 4. CORIOLIS COUPLING CONSTANT AND VIBRATIONAL CHANGES OF THE A CONSTANTS OF SF_4 IN THE ν_4 AND ν_9 STATES

Constants		Frey *et al.*	Levin
$\zeta_{4,9}^{(a)}$		0.670	0.778
$\Delta A_\pm$	ν_4 (MHz)	−22.2	−723
	ν_9 (MHz)	+22.2	+723

Obsd $A_4-A_0=-46.029$ MHz, $A_9-A_0=20.056$ MHz

In the second-order approximation the Coriolis interaction contributes $\Delta A_\pm=\pm D^2/\Delta E$ to the A rotational constant where

$$D = A[(\nu_4/\nu_9)^{1/2}+(\nu_9/\nu_4)^{1/2}]\zeta_{4,9}^{(a)},$$
$$\Delta E = \nu_4-\nu_9,$$

and the + and − signs apply to ν_4 and ν_9, respectively.[10)] Table 4 shows $\Delta A_\pm$ calculated for the two

TABLE 5. ROTATIONAL CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF SF_4 IN THE GROUND STATE (MHz)[a)]

Constants	Obsd: This work	Obsd: Tolles, Gwinn (Ref. 9)
A	6687.737 (11)	6687.71
B	4086.689 (12)	4086.68
C	3219.949 (12)	3219.95

Constants	Obsd: This work	Calcd: Frey *et al.*	Calcd: Levin
τ_{aaaa}	−0.0152 (11)	−0.0160	−0.0167
τ_{bbbb}	−0.0078 (11)	−0.0057	−0.0059
τ_{cccc}	−0.0049 (10)	−0.0034	−0.0032
T_1[b)]	−0.0147 (20)	−0.0153	−0.0138
T_2[b)]	−0.0052 (16)	−0.0027	−0.0031

a) Values in parentheses denote the standard deviations and apply to the last digits. b) See Footnote b) of Table 3.

assignments. The observed A_4 and A_9 constants differ from the ground-state A constant by -46.029 MHz and $+20.056$ MHz, respectively. The $\Delta A_{\pm}$ values for Levin's assignment are obviously too large in magnitude.

Centrifugal Distortion Constants

We remeasured some of the ground-state transitions reported by Tolles and Gwinn, and analyzed them with a few added lines by a least-squares analysis. Table 5 lists the rotational constants and the centrifugal distortion constants thus derived. The rotational constants which were obtained are in very good agreement with those of Tolles and Gwinn. The observed τ constants are compared with those calculated using the force fields mentioned previously. Both assignments give the τ constants which are in fair agreement with the observed.

Discussion and Conclusion

The vibrational satellites of SF_4 in higher excited states would be possible to observe, but it would be very hard to assign the ν_6 and ν_8 satellites, because there are too many lower states including the overtone and combination states of the lower-frequency modes. No information was thus obtained for the two antisymmetric stretching vibrations, but the present work eliminates definitely Levin's assignment for the ν_4 and ν_9 modes.

The computation in the present work was carried out at the Computation Center of Kyushu University.

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