

Abstract

The Doppler-limited spectrum of the $2\nu_1+\nu_3$ band of SF₆ was recorded at 160 and 295 K using a tunable laser difference-frequency spectrometer. The lower temperature eliminates complications from hot bands and reduces the Doppler width, thereby enhancing the resolution and ground-state intensities. An analysis of the band based on an isolated $l = 1 F_{1u}$ mode yields rotational constants in good agreement with those predicted from the ν_1 and ν_3 fundamentals. Small perturbations are observed indicating resonant crossings with nearby vibrations. The X_{11} anharmonic constant is obtained from the band center and previous measurements of ν_1 , ν_3 and $\nu_1+\nu_3$; this is the final parameter needed to calculate the entire $m\nu_1+n\nu_3$ combination ladder.

Doppler-Limited Spectrum and Analysis of the $2\nu_1 + \nu_3$ Band of SF₆

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The Doppler-limited spectrum of the $2\nu_1 + \nu_3$ band of SF₆ was recorded at 160 and 295 K using a tunable laser difference-frequency spectrometer. The lower temperature eliminates complications from hot bands and reduces the Doppler width, thereby enhancing the resolution and ground-state intensities. An analysis of the band based on an isolated $l = 1 F_{1u}$ mode yields rotational constants in good agreement with those predicted from the ν_1 and ν_3 fundamentals. Small perturbations are observed indicating resonant crossings with nearby vibrations. The X_{11} anharmonic constant is obtained from the band center and previous measurements of ν_1 , ν_3 and $\nu_1 + \nu_3$; this is the final parameter needed to calculate the entire $m\nu_1 + n\nu_3$ combination ladder.

INTRODUCTION

Anharmonicity in SF₆ has come under close scrutiny recently as a result of the discovery of isotopically selective multiple photon dissociation of the molecule with intense CO₂ laser radiation (1, 2). It was originally conjectured (3-5) that the initial excitation stages in the ν_3 ladder could be achieved if the anharmonic splittings in a given overtone manifold, governed by Hecht's G_{33} and T_{33} (6), compensated for the normal anharmonic defect, X_{33} . This view was confirmed by an interacting band analysis (7, 8) of the Doppler-limited spectrum of the $3\nu_3$ manifold of SF₆ (9) which yielded the rovibrational constants for the band as well as the anharmonic parameters for the ladder. The job, however, is not finished since it is still necessary to develop a realistic anharmonic potential model for the molecule in order to describe the "quasi continuum" and the dynamic crossover from discrete levels apparent in the multiphoton dissociation process (10, 11). Unfortunately the ν_3 anharmonic constants by themselves are insufficient to specify any particular bond potential. The S-F stretching bond alone affects the ν_1 , ν_2 , and ν_3 modes directly via the symmetry coordinates and is also mixed into ν_4 in the normal mode picture (12). Thus it would be useful to have precise measurements of all the X_{ij} from overtone and combinations of all the SF₆ vibrations to determine the anhar-

monic potential or to compare them with predictions of existing models (13, 14). The present study is sensitive to X_{11} and X_{13} .

Ignoring higher-order anharmonic effects, the entire $m\nu_1 + n\nu_3$ combination ladder is given by

$$[m\nu_1 + n\nu_3, O_h]^0 = m\nu_1^0 + [n\nu_3, O_h]^0 + m(m-1)X_{11} + mnX_{13}, \quad (1)$$

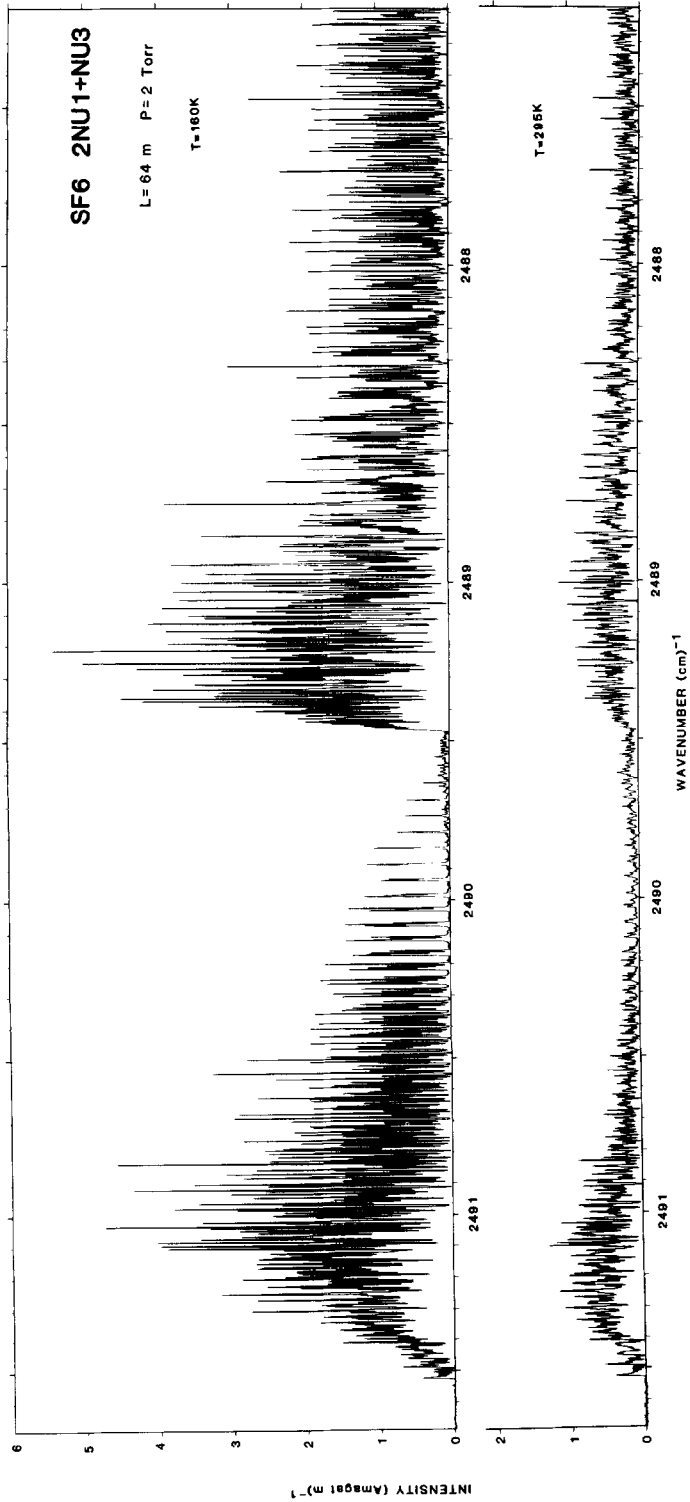
where $[-, O_h]^0$ represents the band center for the O_h symmetry level of the $n\nu_3$ overtone. The fundamental ν_1 band center has been measured quite precisely by Esherick and Owyong (15) using stimulated Raman gain techniques, yielding $\nu_1^0 = 774.5445(10) \text{ cm}^{-1}$. The ν_3 overtone ladder $[n\nu_3, O_h]^0$ has been calculated to $n = 8$ by Patterson *et al.* (8) based on the extremely accurate saturation absorption measurement of the ν_3 fundamental by Bordé *et al.* (16), $\nu_3^0 = 947.976331(6) \text{ cm}^{-1}$, and the Doppler-limited $3\nu_3$ spectrum (7, 9). McDowell (17) has obtained the $\nu_1 + \nu_3$ band origin at $1719.59(3) \text{ cm}^{-1}$ from the unresolved Q-branch head of a Fourier transform spectrum; this yields $X_{13} = -2.9308 \pm 0.03 \text{ cm}^{-1}$ from Eq. (1). In principle X_{11} could be obtained independently of X_{13} by Raman scattering from an overtone of ν_1 . However, this is a very weak effect, so we have chosen to study the infrared-allowed absorption in the $2\nu_1 + \nu_3$ band.

We present here the Doppler-limited spectrum of the $2\nu_1 + \nu_3$ band of SF₆ at 160 and 295 K recorded with a tunable difference-frequency laser spectrometer (9, 18–21). The lower temperature reduces the hot band and high- J spectral components and dramatically increases the intensity of lower- J transitions from the ground vibrational state. The Doppler width is also reduced at low temperatures resulting in a resolution enhancement that is extremely useful in the very dense spectrum. These effects are illustrated in Fig. 1 which compares the complete $2\nu_1 + \nu_3$ spectra at the two temperatures.

The spectrum of $2\nu_1 + \nu_3$ has the appearance of an isolated fundamental-type $l = 1 F_{1u}$ band—at least up to moderate J ($\lesssim 38$). Accordingly, the rovibrational transitions were identified using band contour simulations and were least-squares fit utilizing a noninteracting Hamiltonian. This results in precise effective rotational parameters for comparison to the ν_1 and ν_3 fundamentals and a band origin from which we may calculate X_{11} . Perturbations have been observed as deviations of the spectrum from the model, and we discuss some of the possible resonance crossings of nearby vibrational states. A few selected clean line intensities have been analyzed to determine the band transition moment.

EXPERIMENTAL DETAILS

The spectra of the $2\nu_1 + \nu_3$ band of SF₆ were recorded with a tunable difference-frequency laser spectrometer at MIT Lincoln Laboratory while one of the authors (A.S.P.) was employed there. The system, which mixes an argon laser with a tunable dye laser in LiNbO₃, has been described in detail elsewhere (18–21) and was much the same as for the $3\nu_3$ SF₆ study (9). For the present experiments, however, a higher-precision scanning mode was employed by substituting an actively stabilized ring dye laser (Coherent 699-21) for the older dye laser (Spectra-Physics 370/580) and by sampling the calibration markers on a 10 times finer grid along



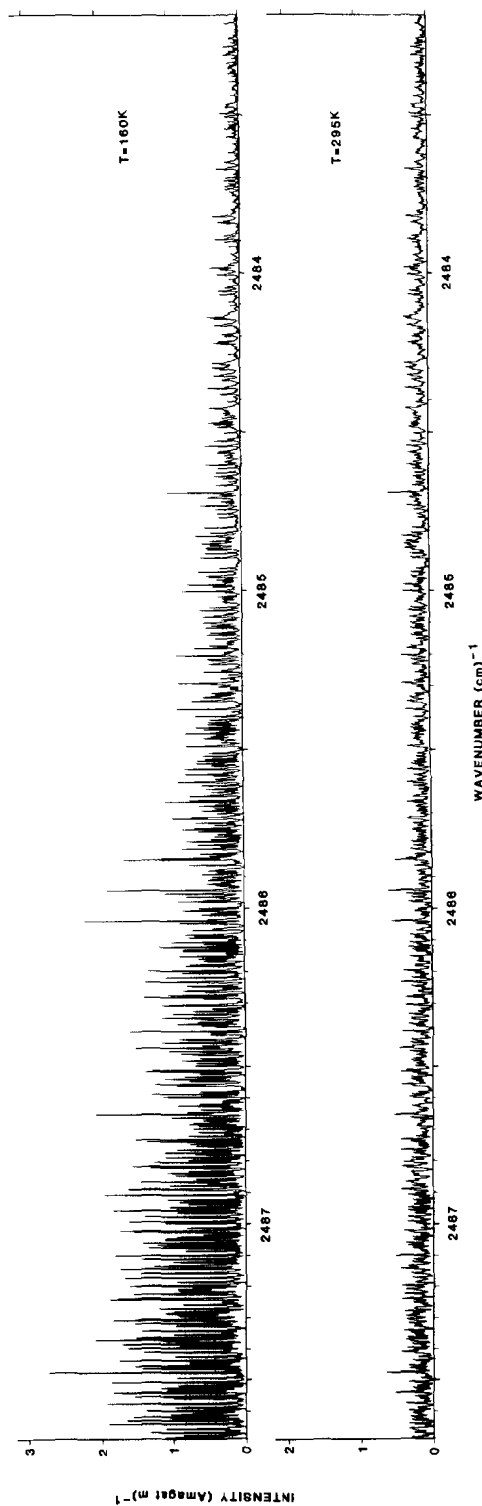


FIG. 1. Comparison of Doppler-limited spectra of $2\nu_1 + \nu_3$ of SF_6 at temperatures of 160 and 295 K. The cell was filled with 2 Torr of SF_6 at 295 K, the overall path length was 64 m.

TABLE I
Observed and Calculated Wavenumbers for the 302 Lines Used in the Fit
for the $2\nu_1 + \nu_3$ Band of SF₆

Line	C(n)	ν_{obs}	Δ^a	Line	C(n)	ν_{obs}	Δ^a
P(36)	E (5)+A1 (3)+F1 (8)	2486.8402	-5	F(26)	F1 (5)+F2 (5)	2487.7214	-1
F(36)	A2 (2)+E (4)+F2 (7)	2486.8893	-6	F(26)	E (3)+A1 (1)+F1 (4)	2487.7362	0
F(36)	F1 (6)+F2 (6)	2486.9083	-8	F(26)	F2 (4)	2487.7479	0
F(37)	E (5)+F2 (8)+F1 (9)	2486.9083	-9	F(26)	E (0)+F1 (0)+F2 (0)	2487.7804	-1
F(36)	E (3)+F1 (5)	2486.9244	-10	F(25)	F1 (0)+F2 (0)	2487.7835	-1
F(35)	F2 (0)+F1 (0)	2486.9317	-1	F(25)	E (0)+F1 (1)+A1 (0)	2487.8010	-1
F(35)	A2 (0)+F2 (1)+E (0)	2486.9573	0	F(25)	F1 (2)+F2 (1)	2487.8152	1
F(36)	A2 (0)+F2 (0)+F1 (0)+A1 (0)	2486.9925	-1	F(25)	A2 (0)	2487.8258	1
F(35)	E (1)+F1 (2)+A1 (0)	2486.9976	-2	F(25)	E (3)+F2 (5)+F1 (6)	2487.8546	-2
F(35)	F2 (3)+F1 (3)	2487.0131	-2	F(24)	E (3)+A1 (2)+F1 (5)	2487.8631	1
F(34)	A2 (2)+E (5)+F2 (8)	2487.0220	2	F(24)	E (3)+A1 (2)+F1 (5)	2487.8631	1
F(34)	F2 (7)+F1 (7)	2487.0470	4	F(24)	F1 (4)+F2 (5)	2487.8795	0
F(34)	E (4)+A1 (2)+F1 (6)	2487.0681	4	F(24)	A2 (1)+F2 (4)	2487.8927	-3
F(35)	E (5)+F2 (8)+F1 (8)	2487.0755	4	F(24)	A2 (0)+F2 (0)	2487.9281	0
F(34)	F1 (5)+F2 (6)	2487.0856	1	F(23)	F1 (0)+F2 (0)	2487.9411	-2
F(34)	A2 (1)	2487.1002	-1	F(23)	A2 (0)+F2 (1)+E (0)	2487.9569	-3
F(33)	E (0)+F1 (1)+A1 (0)	2487.1351	3	F(23)	F1 (1)+F2 (2)	2487.9695	-1
F(34)	A2 (0)	2487.1429	6	F(23)	E (3)+F2 (5)+F1 (5)	2488.0008	-2
F(34)	E (0)+F1 (0)+F2 (0)	2487.1573	4	F(22)	A2 (1)+E (3)+F2 (5)	2488.0184	-1
F(33)	A2 (0)+F2 (2)+E (1)	2487.1723	3	F(22)	F1 (4)+F2 (4)	2488.0333	-3
F(33)	F2 (3)+F1 (3)	2487.1862	2	F(22)	E (2)+F1 (3)	2488.0451	-3
F(32)	E (5)+A1 (2)+F1 (7)	2487.1986	0	F(22)	E (0)+F1 (0)	2488.0728	-1
F(32)	F1 (6)+F2 (7)	2487.2222	4	F(21)	F1 (0)+F2 (0)	2488.0948	0
F(33)	A2 (2)+A1 (2)+F1 (8)+F2 (7)	2487.2393	6	F(21)	E (0)+F1 (1)+A1 (0)	2488.1088	-3
F(32)	A2 (1)+E (4)+F2 (6)	2487.2416	3	F(21)	F2 (1)	2488.1199	-2
F(32)	F1 (5)+F2 (5)	2487.2577	2	F(21)	A2 (1)	2488.1439	-5
F(31)	F1 (0)+F2 (0)	2487.2856	1	F(20)	E (3)+A1 (1)+F1 (4)	2488.1700	0
F(31)	A2 (0)+F2 (1)+E (0)	2487.3079	1	F(20)	F1 (3)+F2 (4)	2488.1834	-1
F(32)	E (0)+F1 (0)+F2 (0)	2487.3183	6	F(20)	E (0)	2488.2141	-4
F(31)	F2 (2)+F1 (1)	2487.3267	2	F(19)	F1 (0)+F2 (0)	2488.2440	-2
F(31)	E (1)+F1 (2)+A1 (0)	2487.3421	3	F(19)	A2 (0)+F2 (1)+E (0)	2488.2567	-2
F(30)	A2 (2)+E (4)+F2 (7)	2487.3714	3	F(19)	E (2)	2488.2838	-4
F(31)	A2 (2)	2487.3847	-1	F(18)	A2 (1)+E (2)+F2 (4)	2488.3171	-2
F(30)	F2 (6)+F1 (6)	2487.3928	2	F(18)	F2 (3)+F1 (3)	2488.3291	-3
F(30)	E (3)+A1 (2)+F1 (5)	2487.4107	2	F(18)	A2 (0)	2488.3526	0
F(30)	F1 (4)+F2 (5)	2487.4254	1	F(17)	F1 (0)+F2 (0)	2488.3895	0
F(29)	F2 (0)+F1 (0)	2487.4557	0	F(17)	E (0)+F1 (1)	2488.4005	-1
F(29)	E (0)+F1 (1)+A1 (0)	2487.4760	-5	F(17)	E (2)	2488.4208	-4
F(29)	F1 (2)+F2 (1)	2487.4936	3	F(16)	E (2)+A1 (1)+F1 (3)	2488.4608	0
F(29)	A2 (0)	2487.5076	2	F(16)	F1 (2)	2488.4709	-4
F(29)	E (4)+F2 (6)+F1 (7)	2487.5530	2	F(16)	A2 (0)	2488.4786	-6
F(28)	F1 (5)+F2 (6)	2487.5593	1	F(16)	E (0)	2488.4884	-2
F(28)	A2 (1)+E (3)+F2 (5)	2487.5756	1	F(48)	A2 (0)+A1 (0)+F1 (0)+F2 (0)	2488.5280	-1
F(28)	F1 (4)+F2 (4)	2487.5888	1	F(15)	F1 (0)+F2 (0)	2488.5311	1
F(27)	F1 (0)+F2 (0)	2487.6218	0	F(49)	A2 (3)+F2 (10)+F1 (11)	2488.5311	-7
F(28)	E (0)+F1 (0)+F2 (0)	2487.6296	2	F(50)	A2 (0)	2488.5311	1
F(27)	A2 (0)+F2 (1)+E (0)	2487.6409	0	F(15)	A2 (0)	2488.5407	3
F(27)	F2 (2)+F1 (1)	2487.6565	1	F(15)	A2 (1)	2488.5552	-5
F(26)	A2 (1)+E (4)+F2 (6)	2487.7053	1	F(14)	A2 (0)+E (2)+F2 (3)	2488.6004	1
F(27)	A2 (2)+F2 (6)	2487.7055	0	F(46)	E (0)+F2 (0)+F1 (0)	2488.6059	0

^a $\Delta = (\nu_{\text{obs}} - \nu_{\text{calc}})$ in units of 10^{-4} cm^{-1} .

with a new line center interpolation routine using a parabolic fit to the upper quarter width of the peaks. This produces an experimental precision of $\sim 5 \times 10^{-5} \text{ cm}^{-1}$ or 1.7 MHz as realized on test N₂O calibration spectra (22). For SF₆, however, perturbations in the spectra did not allow us to fit the transitions to this precision. A complete listing for $2\nu_1 + \nu_3$ of SF₆ is available from the authors (A.S.P.), whereas an abbreviated listing of the isolated, assigned lines used in the present fit is given in Table I.

The SF₆ sample and 2-m base length coolable White cell, run at 64-m total path, were the same as in the $3\nu_3$ experiment (9). The band intensity for $2\nu_1 + \nu_3$ is about half that for $3\nu_3$.

TABLE I—Continued

Line	C(n)	ν_{obs}	Δ^a	Line	C(n)	ν_{obs}	Δ^a
D(47)	E (6)+F1(10)+F2(10)	2488.6091	-2	D(36)	A2(2)+F2(7)+E (4)	2489.1429	-1
F(14)	F1(2)	2488.6091	0	D(42)	A2(3)+F2(10)+E (6)	2489.1519	0
F(14)	E (6)	2488.6211	0	D(33)	A2(0)+E (1)+F2(2)	2489.1557	-2
D(45)	A2(3)+F2(10)+F1(11)+A1(3)	2488.6434	0	D(27)	A2(2)+F2(6)	2489.1737	1
F(13)	F1(0)+F2(0)	2488.6690	6	D(31)	E (1)+A1(0)+F1(2)	2489.1870	1
F(13)	E (0)	2488.6767	4	D(26)	E (0)+F2(0)+F1(0)	2489.1952	-1
F(13)	E (1)	2488.6865	3	D(35)	A2(0)+E (0)+F2(1)	2489.1982	-5
F(12)	E (1)+A1(1)+F1(2)	2488.7361	4	D(32)	A2(1)+F2(6)+E (4)	2489.2015	-4
D(42)	A2(0)+A1(0)+F1(0)+F2(0)	2488.7509	0	D(30)	F2(5)+F1(4)	2489.2015	-4
F(12)	F1(0)	2488.7509	1	D(38)	A2(2)+F2(9)+E (6)	2489.2070	-3
D(48)	A2(2)+F2(7)	2488.7509	-2	D(25)	E (3)+F2(5)	2489.2160	0
F(11)	F1(0)+F2(0)	2488.8015	-4	D(33)	E (0)+A1(0)+F1(1)	2489.2250	-2
F(11)	E (1)	2488.8148	-3	D(30)	E (3)+F1(5)+A1(2)	2489.2290	-3
D(40)	A2(0)	2488.8532	-2	D(24)	A2(0)	2489.2363	2
F(10)	A2(0)	2488.8680	6	F(4)	E (0)	2489.2395	1
F(10)	E (0)	2488.8778	6	D(29)	F1(2)+F2(1)	2489.2423	-2
D(38)	E (0)+F2(0)+F1(0)	2488.8823	0	D(27)	E (1)	2489.2446	-3
D(43)	A2(1)+E (2)+F2(4)	2488.9041	0	F(31)	A2(0)+E (0)+F2(1)	2489.2498	-6
D(37)	E (5)+F1(9)+F2(0)	2488.9131	1	D(28)	A2(1)+F2(5)+E (3)	2489.2553	-1
F(9)	F2(0)	2488.9321	4	D(30)	F1(6)+F2(6)	2489.2621	-3
D(48)	A2(3)+F2(10)+E (6)	2488.9321	-2	D(23)	A2(1)	2489.2797	0
D(45)	A2(0)+E (1)+F2(2)	2488.9406	-1	D(26)	E (3)+F1(4)+A1(1)	2489.2797	-3
F(9)	A2(0)	2488.9406	4	D(27)	A2(0)+E (0)+F2(1)	2489.2964	-2
D(36)	A2(0)+A1(0)+F1(0)+F2(0)	2488.9434	5	D(24)	A2(1)	2489.3034	0
D(42)	A2(2)+F2(7)+E (4)	2488.9601	0	D(26)	F1(5)+F2(5)	2489.3071	-2
D(43)	E (1)+A1(0)+F1(2)	2488.9803	1	D(25)	E (0)+A1(0)+F1(1)	2489.3174	-3
D(45)	F1(2)+F2(1)	2488.9902	3	D(28)	E (4)+F1(6)+A1(2)	2489.3218	1
D(39)	A2(1)	2488.9902	0	D(27)	F2(0)+F1(0)	2489.3309	-3
D(34)	E (0)+F2(0)+F1(0)	2489.0003	1	D(23)	A2(0)+E (0)+F2(1)	2489.3373	-3
D(40)	E (4)+F1(6)+A1(2)	2489.0003	1	D(21)	E (0)+A1(0)+F1(1)	2489.3564	3
D(41)	A2(0)+E (1)+F2(2)	2489.0184	3	D(19)	A2(0)+F2(1)	2489.3736	2
D(36)	A2(1)	2489.0279	-1	D(15)	A2(1)	2489.3766	1
D(33)	A2(2)+F2(7)+F1(8)+A1(2)	2489.0279	5	D(20)	E (3)+F1(4)+A1(1)	2489.3891	-1
D(38)	A2(1)+F2(6)+E (4)	2489.0389	0	D(19)	F1(0)+F2(0)	2489.3964	3
D(42)	E (5)+F1(8)+A1(3)	2489.0446	4	D(18)	A2(1)+F2(4)+E (2)	2489.4029	2
D(32)	E (0)+F2(0)+F1(0)	2489.0543	4	D(15)	F2(0)+F1(0)	2489.4206	-2
D(39)	E (1)+A1(0)+F1(2)	2489.0543	-4	D(14)	A2(0)+F2(3)+E (2)	2489.4265	2
F(7)	F2(0)	2489.0579	3	D(10)	A2(0)	2489.4449	5
F(7)	E (0)	2489.0621	5	D(9)	F2(0)	2489.4489	4
D(36)	E (3)+F1(5)	2489.0762	0	D(3)	A2(0)	2489.4637	2
D(43)	A2(0)+E (0)+F2(1)	2489.0791	5	F(2)	E (0)+F2(0)	2489.6314	1
D(40)	A2(2)+F2(8)+E (5)	2489.0791	6	F(2)	F2(0)+E (0)	2489.6314	0
D(31)	E (4)+F1(7)+F2(7)	2489.0791	-5	F(3)	A2(0)	2489.6844	-1
D(33)	A2(1)	2489.0853	3	F(4)	E (0)	2489.7359	-1
D(37)	A2(0)+E (1)+F2(2)	2489.0899	0	F(5)	F2(0)	2489.7871	4
D(34)	F2(4)	2489.0899	-1	F(6)	A2(0)	2489.8364	-3
D(30)	A2(0)+F2(0)	2489.1049	4	F(7)	A2(0)	2489.8874	-3
D(38)	E (5)+F1(7)+A1(2)	2489.1116	1	F(8)	E (1)+F1(1)	2489.9329	3
D(44)	E (7)+F1(10)+A1(3)	2489.1230	9	F(8)	F1(0)	2489.9368	0
D(29)	E (4)+F1(7)+F2(6)	2489.1284	1	F(9)	F1(0)+F2(0)	2489.9797	-3

ASSIGNMENT AND ANALYSIS

The transition frequencies for the $2\nu_1 + \nu_3$ band of SF₆ may be expressed in the same form as those for a dipole-active fundamental of a spherical-top molecule. In the diagonal approximation the *P*-, *Q*-, and *R*-branch transitions may be written (6, 23, 24)

$$\nu_P(J, C(N)) = m - nJ + pJ^2 - qJ^3 + \dots + [g + hJ + \dots]P_4, \quad (2a)$$

$$\nu_Q(J, C(N)) = m + vJ(J+1) + wJ^2(J+1)^2 + \dots$$

$$+ [-2g + uJ(J+1) - \dots]Q_4, \quad (2b)$$

$$\nu_R(J, C(N)) = m + n(J+1) + p(J+1)^2 + q(J+1)^3 + \dots$$

$$+ [g - h(J+1) + \dots]R_4, \quad (2c)$$

TABLE I—Continued

Line	C(n)	ν_{obs}	Δ^a	Line	C(n)	ν_{obs}	Δ^a
R(9)	E(0)	2489.9833	-1	R(26)	A2(1)+E(4)+F2(6)	2490.6297	4
R(9)	F1(2)	2489.9857	1	R(26)	F2(5)+F1(5)	2490.6450	1
R(10)	A2(0)+F2(2)	2490.0257	-4	R(27)	F2(0)+F1(0)	2490.6586	-1
R(11)	F1(0)+F2(0)	2490.0707	-1	R(25)	E(3)+F1(6)	2490.6624	0
R(11)	A2(0)	2490.0755	0	R(26)	F1(3)	2490.6686	3
R(12)	E(1)+A1(1)+F1(2)	2490.1147	-2	R(27)	F2(2)+F1(1)	2490.6886	0
R(12)	A2(0)	2490.1259	0	R(26)	E(0)+F1(0)	2490.6991	6
R(13)	F1(0)+F2(0)	2490.1577	-3	R(28)	F1(5)+F2(6)	2490.7047	4
R(13)	E(0)+F1(1)	2490.1641	-2	R(28)	A2(1)+E(3)+F2(5)	2490.7190	5
R(13)	E(1)	2490.1718	-5	R(30)	A2(2)+E(4)+F2(7)	2490.7416	3
R(14)	A2(0)+E(2)+F2(3)	2490.1998	-4	R(29)	A2(0)	2490.7603	5
R(14)	F2(2)	2490.2068	-3	R(28)	E(0)+F1(0)+F2(0)	2490.7688	2
R(14)	E(0)	2490.2166	-4	R(31)	A2(0)+F2(1)+E(0)	2490.7663	4
R(15)	F2(0)+F1(0)	2490.2409	-3	R(32)	E(5)+A1(2)+F1(7)	2490.7918	4
R(15)	A2(0)	2490.2486	-2	R(30)	A2(1)	2490.7999	2
R(15)	E(1)	2490.2568	-2	R(29)	E(4)+F2(6)+F1(7)	2490.8029	3
R(16)	E(2)+A1(1)+F1(3)	2490.2512	-2	R(31)	E(1)+F1(2)+A1(0)	2490.8161	-2
R(16)	F2(3)+F1(2)	2490.2896	-2	R(32)	A2(1)+E(4)+F2(6)	2490.8286	3
R(16)	E(0)	2490.3041	-4	R(32)	F1(5)+F2(5)	2490.8433	4
R(17)	F1(0)+F2(0)	2490.3203	-3	R(33)	A2(0)+F2(2)+E(1)	2490.8694	7
R(17)	E(0)+F1(1)	2490.3294	-2	R(35)	A2(0)+F2(1)+E(0)	2490.8816	4
R(17)	E(2)	2490.3468	-4	R(34)	F1(5)+F2(6)	2490.8929	-5
R(18)	A2(1)+E(2)+F2(4)	2490.3586	-2	R(32)	E(0)+F1(0)+F2(0)	2490.9007	4
R(18)	F2(3)+F1(3)	2490.3685	0	R(34)	A2(1)+E(3)+F2(5)	2490.9074	4
R(18)	E(1)	2490.3758	-3	R(38)	A2(2)+E(6)+F2(9)	2490.9182	-3
R(19)	F1(0)+F2(0)	2490.3959	-1	R(37)	E(0)+F1(1)+A1(0)	2490.9229	-2
R(19)	A2(0)+F2(1)+E(0)	2490.4064	-1	R(36)	A2(2)+E(4)+F2(7)	2490.9229	3
R(19)	F1(1)	2490.4144	0	R(33)	A2(2)+A1(2)+F1(8)+F2(7)	2490.9318	4
R(19)	E(2)	2490.4302	-1	R(39)	F2(0)+F1(0)	2490.9362	-2
R(20)	F1(3)+F2(4)	2490.4434	-2	R(36)	F1(6)+F2(6)	2490.9402	2
R(20)	A2(0)	2490.4521	-4	R(36)	E(3)+A1(2)+F1(5)	2490.9549	1
R(21)	F2(0)+F1(0)	2490.4677	1	R(37)	A2(0)+F2(2)+E(1)	2490.9620	2
R(20)	E(0)	2490.4705	-3	R(37)	F1(3)+F2(3)	2490.9775	2
R(21)	F1(1)+E(0)+A1(0)	2490.4795	0	R(35)	E(5)+F2(8)+F1(8)	2490.9910	-4
R(21)	F2(1)	2490.4889	-1	R(38)	A2(1)+E(4)+F2(6)	2490.9989	0
R(22)	A2(1)+E(3)+F2(5)	2490.5022	4	R(40)	A2(2)+E(5)+F2(8)	2491.0011	-1
R(21)	A2(1)	2490.5105	-3	R(36)	A2(0)+F2(0)+F1(0)+A1(0)	2491.0207	3
R(22)	F2(4)+F1(4)	2490.5148	2	R(37)	A2(2)	2491.0335	3
R(22)	E(2)+F1(3)	2490.5248	1	R(46)	A2(3)+F2(11)+E(7)	2491.0335	-1
R(23)	A2(0)+F2(1)+E(0)	2490.5490	4	R(41)	A2(0)+F2(2)+E(1)	2491.0385	-8
R(23)	F1(1)+F2(2)	2490.5595	1	R(37)	E(5)+F2(8)+F1(9)	2491.0479	-6
R(23)	E(1)	2490.5678	2	R(38)	E(1)+F2(1)	2491.0597	-2
R(23)	A2(1)	2490.5761	0	R(47)	A2(0)+F2(1)+E(0)	2491.0737	0
R(23)	E(3)+F1(5)	2490.5880	1	R(39)	E(5)+F2(8)+F1(8)	2491.0860	-1
R(24)	A2(1)+E(2)+F2(4)	2490.5933	1	R(40)	A2(0)	2491.1113	0
R(25)	F2(0)+F1(0)	2490.5993	4	R(46)	A2(2)+E(5)+F2(8)	2491.1358	-2
R(24)	E(1)	2490.6092	-3	R(41)	E(6)+F2(9)+F1(10)	2491.1543	0
R(25)	E(0)+F1(1)+A1(0)	2490.6140	2	R(46)	E(4)	2491.1725	-4
R(24)	E(0)	2490.6168	-1	R(42)	A2(0)+F2(0)+F1(0)+A1(0)	2491.1783	-6
R(24)	A2(0)+F2(0)	2490.6256	3	R(43)	A2(3)+F1(9)+F2(9)	2491.1831	-7
				R(44)	E(0)+F1(0)+F2(0)	2491.2263	2
				R(46)	A2(0)+F2(1)	2491.2499	4

where C designates the octahedral symmetry species with the counting index N for repeated species within each ground-state angular momentum J manifold. Note that the band parameters m and n should not be confused with the integer indices for the combination ladder given in Eq. (1). The P_4 , Q_4 , and R_4 terms are related to the symmetry-adapted fourth-rank tensor coefficients of Moret-Bailly (23) which have been calculated (25) for all $C(N)$ up to $J = 150$.

Although the above formulas are sufficiently accurate to make line assignments for $J \leq 30$, it is necessary for higher J assignments to calculate the "off-diagonal" corrections (26) resulting from the interaction of Coriolis sublevels. Using these corrections to Eq. (2), we are able to extend the assignments up to $J \sim 50$ in the R and Q branches and up to $J \sim 38$ in the P branch.

The P -branch assignments break down at $J = 38$, presumably because a resonance strongly perturbs the levels. Because assignments are made iteratively with J , we

TABLE II
Rovibrational Constants (cm⁻¹) for $2\nu_1 + \nu_3$ of SF₆

Fit to R and Q branches	Estimated from ν_1 [15] and ν_3 [16]
$m = 2489.4682(1)$	
$n = 0.055617(8)$	0.0558173(4)
$p = -4.099(2) \times 10^{-4}$	$-3.8229(4) \times 10^{-4}$
$v = -3.033(2) \times 10^{-4}$	$-2.9063(6) \times 10^{-4}$
$w = -2.31(7) \times 10^{-9}$	
$g = -2.4613(8) \times 10^{-5}$	$-2.4562(3) \times 10^{-5}$
Fit to P branch	
$n = 0.055628(22)$	
$p = 3.80(2) \times 10^{-4}$	
$q = 8.9(3) \times 10^{-7}$	

were not able to pick up the identifications at higher J to determine if the resonance is a local crossing. This perturbation, however, does weakly affect the lower J transitions in the P branch, so we found it necessary to fit the P -branch n , p , and q parameters of Eq. (2a) separately from the R -branch parameters of Eq. (2c). The fact that the perturbation does not affect the tensor constants, g , indicates that an F_{1u} - F_{1u} type Fermi or Coriolis resonance is operative. Such an interaction is most likely due to a resonance with the $2\nu_3 + \nu_4$ band expected at ~ 2505 cm⁻¹. The fact that the P branch is more strongly perturbed than the R branch also indicates a crossing from a band at higher frequency.

In Table I we give the 302 assigned lines used in the least-squares fit to the corrected Eqs. (2). These lines were chosen because they are unblended except for unresolved "clusters" with splittings less than ~ 0.0003 cm⁻¹. Only the species $C(N)$ with the largest statistical weight in the cluster was used in the fit and these are listed first in the Table for a given frequency. Only species clustered to within 0.0001 cm⁻¹ of the calculated frequencies are listed.

The fit resulted in the determination of nine spectroscopic constants as shown in Table II. Higher-order constants were set to zero if they could not be determined with statistical significance. The q parameter in the P branch is necessary to fit transitions in the perturbation region near $J = 38$. The overall standard deviation of the fit for the 302 lines was 3.2×10^{-4} cm⁻¹ or about 1/6 the Doppler width of 1.9×10^{-3} cm⁻¹.

Also shown in Table II is a comparison of the $2\nu_1 + \nu_3$ constants with those expected from the fundamentals. For example, v and p in $2\nu_1 + \nu_3$ should be equal to v and p in the ν_3 band (16) plus $2(B_1 - B_0)$ from the ν_1 band. A stimulated Raman gain measurement of ν_1 by Esherick and Owyong (15) yielded $(B_1 - B_0) = -1.1038(4) \times 10^{-4}$ cm⁻¹. They also observed no octahedral splittings in ν_1 which accounts for the agreement in the g parameters between ν_3 and $2\nu_1 + \nu_3$.

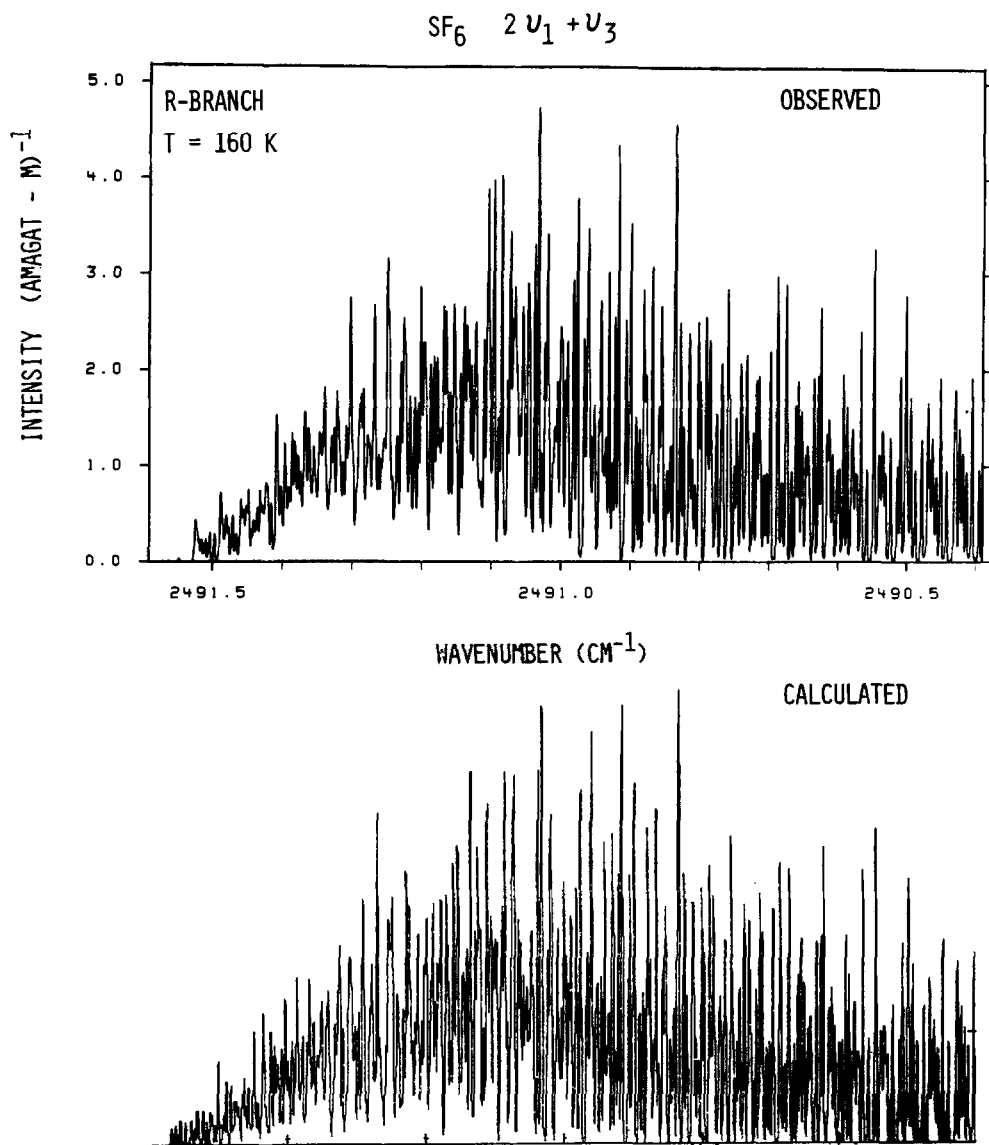


FIG. 2. Comparison of observed and calculated spectrum of $2\nu_1 + \nu_3$ of SF_6 at 160 K. High- J R branch.

Finally from our $2\nu_1 + \nu_3$ band origin, m , and prior measurements of ν_1^0 (15), ν_3^0 (16), and $(\nu_1 + \nu_3)^0$ (17), we obtain $X_{11} = -0.8677 \pm 0.03 \text{ cm}^{-1}$ from Eq. (1). The large uncertainty in this value reflects the coarse X_{13} value from the low-resolution measurement of $\nu_1 + \nu_3$ (17).

LINE INTENSITIES AND TRANSITION DIPOLE MOMENT

The dipole transition moment of $2\nu_1 + \nu_3$ can be derived from the rovibrational peak absorption coefficients, k_{if} , exactly as for the case of a spherical-top funda-

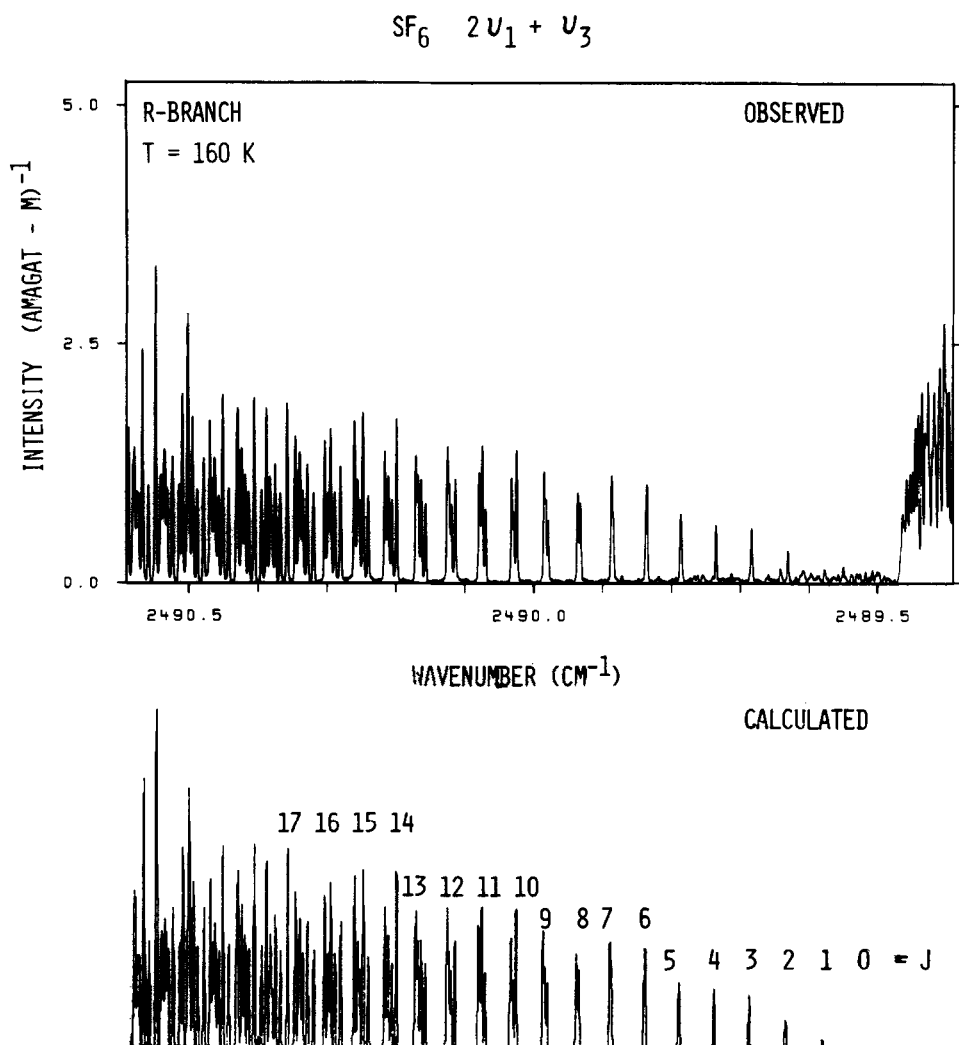


FIG. 3. Comparison of observed and calculated spectrum of $2\nu_1 + \nu_3$ of SF_6 at 160 K. Low- J R branch

mental. The peak and integrated line intensity for a Gaussian Doppler-limited line are related by

$$S_{if} = k_{if}\gamma_D[\pi/4 \ln 2]^{1/2}/a, \quad (3)$$

where $\gamma_D = 0.716 \times 10^{-6} \nu_{if}[T/M]^{1/2}$ is the Doppler FWHM, and $a = 0.95$ is the isotopic abundance of $^{32}\text{SF}_6$. Here T is in Kelvin and M is the mass number. The line strength is given by (27)

$$S_{if} = (8\pi^3 N_0/3hcZ)\nu_{if}\mu_{113}^2\epsilon_c(2J_f + 1) \times e^{-B_0hcJ_i(J_i+1)/kT}(1 - e^{-h\nu_{if}/kT}). \quad (4)$$

Here $N_0 = 2.687 \times 10^{19}$ molecules/ cm^2 is Loschmidt's number, $Z = Z_V Z_R$ is the product of the vibrational and rotational partition functions and ν_{if} is the transition wavenumber. The units of Eq. (4) are $\text{cm}^{-2} \text{Amagat}^{-1}$ while those of k_{if} are cm^{-1}

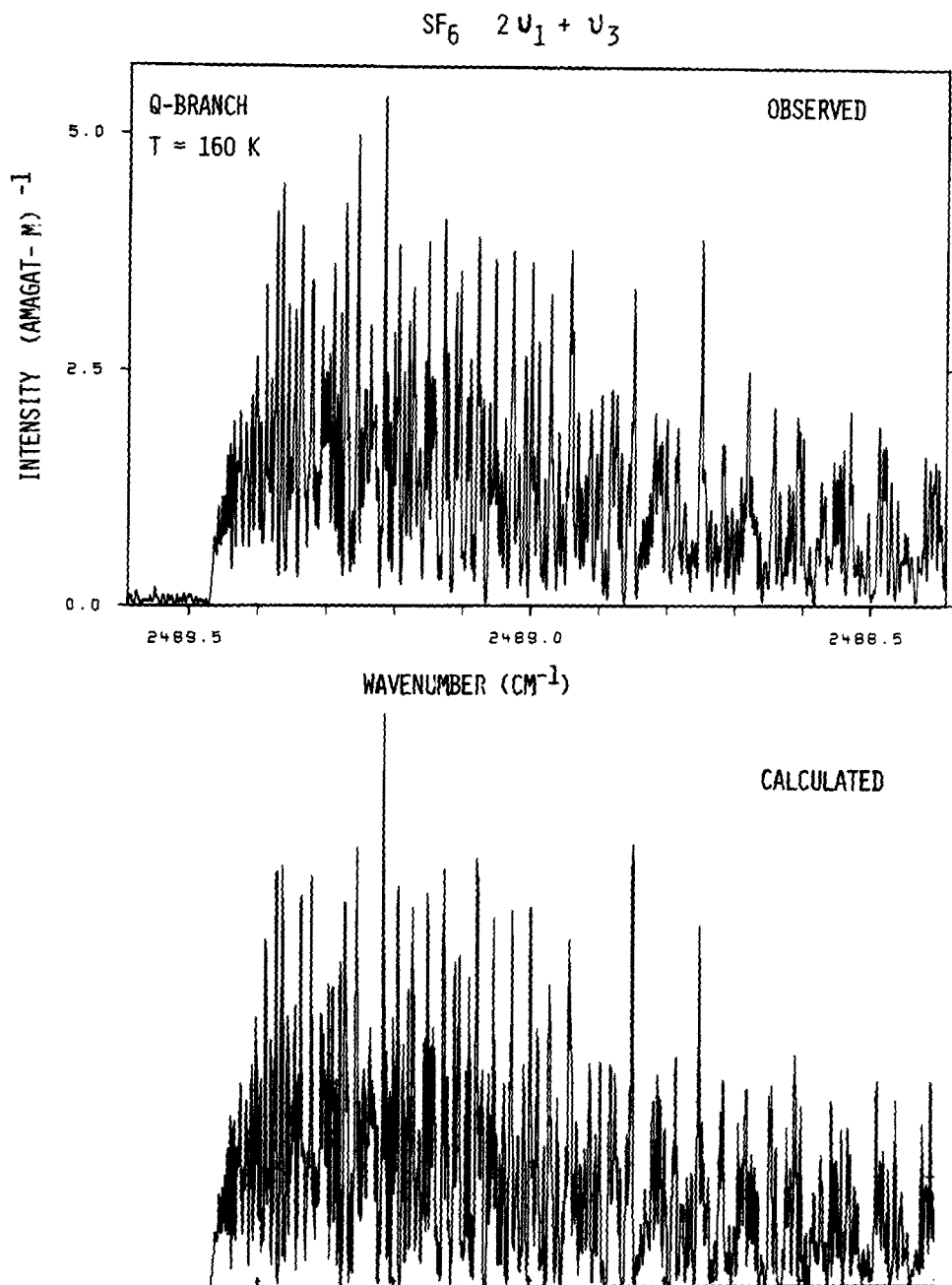


FIG. 4. Comparison of observed and calculated spectrum of $2\nu_1 + \nu_3$ of SF_6 at 160 K. Q branch.

Amagat⁻¹ when μ_{113} is expressed in Debye ($1 \text{ D} = 10^{-18} \text{ esu-cm}$). The nuclear spin statistical weights are $\epsilon_c = 2, 10, 8, 6, 6$ for species $C = A_1, A_2, E, F_1, F_2$, respectively. At 160 K the rotational partition function is approximately (12, 27)

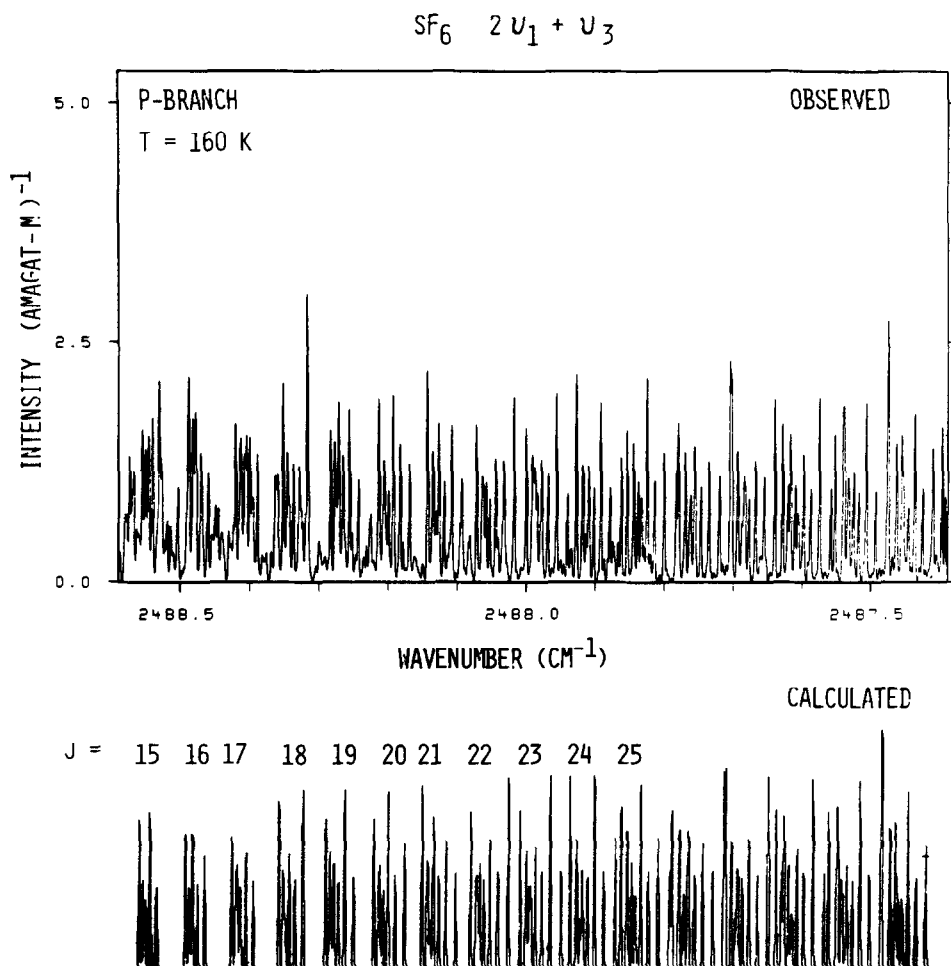


FIG. 5. Comparison of observed and calculated spectrum of $2\nu_1 + \nu_3$ of SF_6 at 160 K. Mid- J P branch

$$Z_R \approx (8\pi^{1/2}/3)(B_0hc/kT)^{-3/2} = 2.016 \times 10^5, \quad (5)$$

and the vibrational partition function is

$$Z_V \approx \prod_{i=1}^6 (1 - e^{-h\nu_i^0/kT})^{-d_i} = 1.202, \quad (6)$$

where d_i is the degeneracy of the vibration, ν_i .

In Figs. 2-6 we compare the observed absorption spectrum of $2\nu_1 + \nu_3$ of SF_6 at 160 K normalized by Beer's law to the calculated intensity spectrum using the constants of Table II in the model of Eq. (2) and relative strengths from Eq. (4). The correspondence is quite good for $J \lesssim 50$ in the R and Q branches and for $J \lesssim 38$ in the P branch. At higher J , overlap, blending, and perturbations make assignment and fitting more difficult.

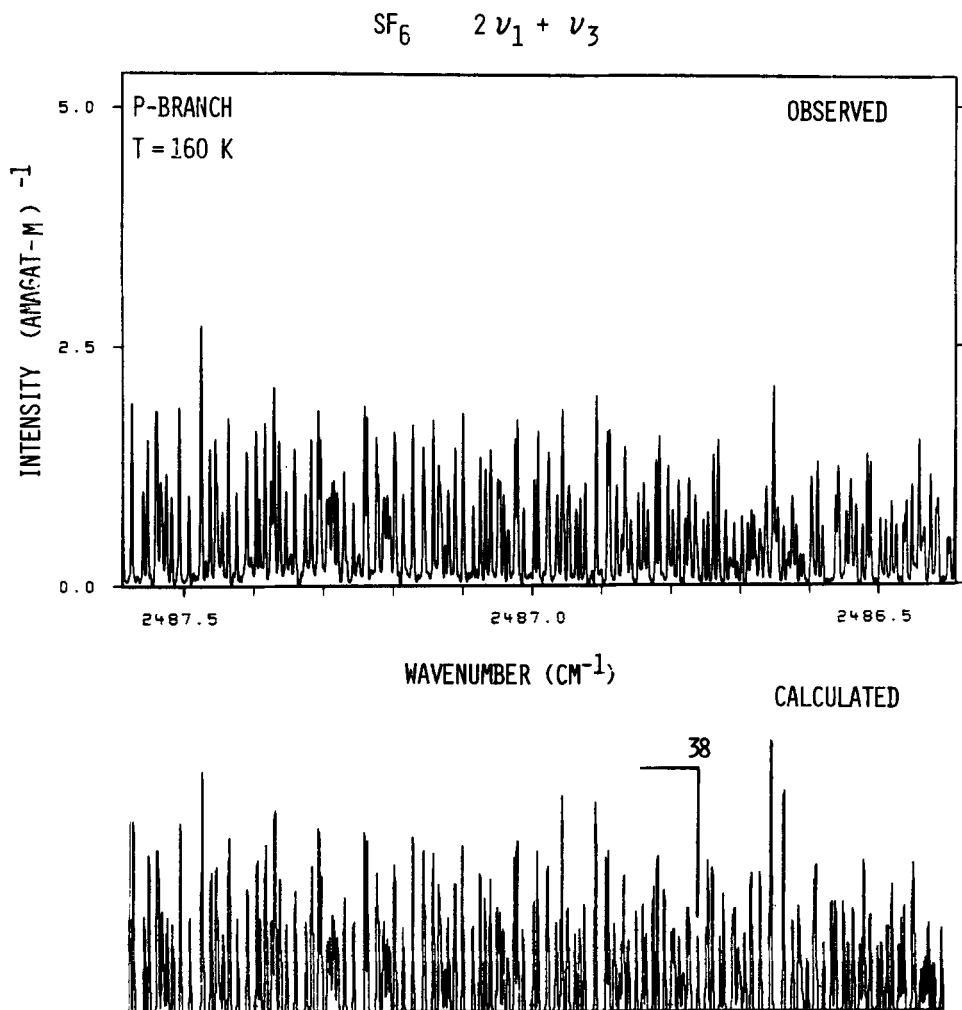


FIG. 6. Comparison of observed and calculated spectrum of $2\nu_1 + \nu_3$ of SF_6 at 160 K. High- J P branch.

The transition moment μ_{113} was computed according to Eqs. (3)–(6) for nine isolated line clusters in the P and R branches selected to be reasonably free of blending. Lines in the very dense Q branch, high- J R branch, and low- and high- J P branch were not chosen because of the high probability of blending. The results given in Table III indicate an average transition moment of $\mu_{113} = 7.1 \times 10^{-4}$ D and a spread of $\pm 3\%$. This variation is expected experimentally from baseline uncertainties and residual blending. The absolute dipole moment additionally suffers from systematic experimental errors in the cell temperature, path length, fill pressure, and sample purity. The overall estimated errors then are $\sim \pm 5\%$ for μ_{113} and about twice that for the corresponding integrated band strength, $S_{113} = 1.70 \times 10^{-5} \text{ cm}^{-2} \text{ Amagat}^{-1}$ (28).

TABLE III

Dipole Transition Moments for Selected Rovibrational Lines of $2\nu_1 + \nu_3$ of SF₆

Line	ν_{if} (cm ⁻¹)	$ u_{113} $ (Debye x 10 ⁴)
P(23) A ₂ (0) + E(0) + F ₂ (1)	2487.9569	7.20
P(22) A ₂ (1) + E(3) + F ₂ (5)	2488.0184	7.15
P(19) A ₂ (0) + E(0) + F ₂ (1)	2488.2567	7.04
P(15) A ₂ (0) + E(0) + F ₂ (1)	2488.5407	7.29
R(8) A ₁ (0) + E(1) + F ₁ (1)	2489.9329	7.28
R(10) A ₂ (0) + E(1) + F ₂ (2)	2490.0257	7.10
R(14) A ₂ (0) + E(2) + F ₂ (3)	2490.1998	6.97
R(18) A ₂ (1) + E(2) + F ₂ (4)	2490.3586	6.93
R(20) A ₂ (0) + E(0) + F ₂ (1)	2490.4521	6.93

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