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Microwave Spectrum and Centrifugal Distortion Effects of Thionyl Fluoride

Ichiro YAMAGUCHI, Osamu OHASHI, Hirotaka TAKAHASHI, Takeshi SAKAIZUMI, and Masao ONDA
Department of Chemistry, Faculty of Science and Technology, Sophia University, Tokyo 102
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Ferguson analysed the microwave spectrum of thionyl fluoride and obtained the structure and dipole moment of the molecule.[1] Assignment of the spectral lines was so made that the low J R-branch lines fit the frequencies calculated from the rigid molecular model. The reported frequencies, however, do not coincide with the calculated values in a high J range. The larger the J value, the greater the deviation; *e. g.*, for the line $12_{93}\leftarrow12_{94}$ the deviation is as large as 11.44 MHz. The centrifugal distortion effect is expected to account for the deviation. In this paper we report on several series of Q-branches newly observed for the normal species $^{32}S^{16}O^{19}F_2$, and the analyses of the spectrum taking into account the centrifugal distortion effect.

Thionyl fluoride was synthesized by the reaction of thionyl chloride with antimony(III) fluoride.[2] Conventional microwave spectrometers were used with 100 kHz Stark modulation. The sample pressure was 0.01—0.015 mmHg and the spectrum was observed at dry ice and room temperatures. The frequency range observed was 8.0—36.0 GHz.

The observed transition frequencies are given in Table 1. Spectral analysis was made on the basis of Watson's formula for the centrifugal distortion effect.[3] Thionyl fluoride molecule has C_s symmetry. It may therefore be inappropriate to account for the observed deviations by considering the first order perturbation terms only. However, it can be seen from the table that the deviation of observed frequencies from the calculated ones obtained by the least squares fit with Watson's formula is very small throughout, and the higher order terms were therefore neglected.

The transition frequencies calculated from the rigid rotor model with the rotational constants given by Ferguson were the first reference to the assignment of the observed lines. However, deviations of the observed frequencies were apparent from the rigid rotor model frequencies. It was worthwhile to divide the lines into several series, each having a specific set of K_{-1} and K_{+1} (Table 1). The observed frequencies in a series, when appropriately assigned, showed a regular variation of the deviation with changing J value, which greatly helped in obtaining the final assignment. The assigned lines were used for the least squares fit of transition frequency. This process was continued until most of the observed frequencies coincide with the calculated ones, the centrifugal corrections also being shown in Table 1.

The effective rotational constants and centrifugal distortion coefficients thus obtained are shown in Table 2, together with the rotational constants given by Ferguson.

In our assignments of many spectral lines, taking into account the centrifugal distortion effect, we found some misassignments made by Ferguson. Examples are given in Fig. 1, where the spectra (a) observed, (b) calculated for a model with centrifugal distortion

1) R. C. Ferguson, *J. Amer. Chem. Soc.*, **76**, 850 (1954).
2) H. Booth and F. C. Mericola, *ibid.*, **62**, 640 (1940).
3) J. K. G. Watson, *J. Chem. Phys.*, **45**, 1360 (1966).

Table 1. Observed transition frequencies and centrifugal distortion effect (in MHz)

Transition	ν_{obsd} a)	$\nu_{obsd}-\nu_{calcd}$	Centrifugal b) correction
* $1_{10} \leftarrow 0_{00}$	16971.72	0.00	−0.04
* $2_{11} \leftarrow 1_{01}$	33685.48	0.04	−0.40
* $2_{20} \leftarrow 1_{10}$	33957.30	−0.01	−0.30
* $2_{21} \leftarrow 1_{11}$	34201.06	−0.04	−0.13
* $2_{11} \leftarrow 1_{10}$	30023.61	0.02	−0.45
* $3_{03} \leftarrow 2_{02}$	33254.98	−0.39	−0.26
* $3_{13} \leftarrow 2_{12}$	33242.12	0.39	−0.29
$J_{J-1,1} \leftarrow J_{J-1,2}$			
$2_{11} \leftarrow 2_{12}$	10211.78	−0.10	−0.40
$3_{21} \leftarrow 3_{22}$	9833.88	−0.10	−0.81
$4_{31} \leftarrow 4_{32}$	9336.83	0.00	−1.26
$5_{41} \leftarrow 5_{42}$	8727.72	0.04	−1.69
$6_{51} \leftarrow 6_{52}$	8017.63	0.09	−2.00
$J_{J,1} \leftarrow J_{J-2,2}$			
$2_{21} \leftarrow 2_{02}$	10999.56	0.04	0.06
$3_{31} \leftarrow 3_{12}$	11450.76	0.09	0.04
$4_{41} \leftarrow 4_{22}$	12120.18	0.05	−0.06
$5_{51} \leftarrow 5_{32}$	13059.21	0.04	−0.42
$6_{61} \leftarrow 6_{42}$	14319.88	−0.01	−1.33
$7_{71} \leftarrow 7_{52}$	15945.86	−0.02	−3.26
$8_{81} \leftarrow 8_{62}$	17964.68	−0.01	−6.82
$9_{91} \leftarrow 9_{72}$	20384.98	−0.07	−12.70
$10_{10,1} \leftarrow 10_{82}$	23198.52	0.01	−21.68
$11_{11,1} \leftarrow 11_{92}$	26382.98	−0.07	−34.57
$12_{12,1} \leftarrow 12_{10,2}$	29906.00	−0.05	−52.18
$13_{13,1} \leftarrow 13_{11,2}$	33726.06	0.05	−75.28
$J_{J-2,2} \leftarrow J_{J-2,3}$			
$3_{12} \leftarrow 3_{13}$	17602.39	−0.18	−0.57
* $4_{22} \leftarrow 4_{23}$	17501.15	−0.10	−1.27
* $5_{32} \leftarrow 5_{33}$	17305.39	−0.10	−2.18
* $6_{42} \leftarrow 6_{43}$	16980.32	−0.10	−3.23
$7_{52} \leftarrow 7_{53}$	16498.74	−0.02	−4.27
$8_{62} \leftarrow 8_{63}$	15846.78	0.00	−5.15
$9_{72} \leftarrow 9_{73}$	15025.59	−0.12	−5.66
$10_{82} \leftarrow 10_{83}$	14049.12	0.00	−5.66
$11_{92} \leftarrow 11_{93}$	12938.99	0.02	−5.02
$12_{10,2} \leftarrow 12_{10,3}$	11722.67	0.03	−3.64
$13_{11,2} \leftarrow 13_{11,3}$	10431.60	−0.01	−1.49
$14_{12,2} \leftarrow 14_{12,3}$	9101.33	0.05	1.40
$J_{J-1,2} \leftarrow J_{J-3,3}$			
$3_{22} \leftarrow 3_{03}$	17673.53	0.18	−0.41
$4_{32} \leftarrow 4_{13}$	17713.75	0.20	−0.83
$5_{42} \leftarrow 5_{23}$	17798.06	0.08	−1.29
$6_{52} \leftarrow 6_{33}$	17952.08	0.08	−1.76
$J_{J-3,3} \leftarrow J_{J-3,4}$			
* $7_{43} \leftarrow 7_{44}$	24553.88	−0.09	−4.61
$8_{53} \leftarrow 8_{54}$	24419.44	−0.16	−6.28
$9_{63} \leftarrow 9_{64}$	24205.04	−0.09	−8.11
$10_{73} \leftarrow 10_{74}$	23879.74	0.13	−9.98
$11_{83} \leftarrow 11_{84}$	23409.74	0.02	−11.68
$12_{93} \leftarrow 12_{94}$	22765.10	−0.02	−12.88
$13_{10,3} \leftarrow 13_{10,4}$	21924.72	0.03	−13.23
$14_{11,3} \leftarrow 14_{11,4}$	20881.38	−0.02	−12.42
$J_{J-2,3} \leftarrow J_{J-4,4}$			
$7_{53} \leftarrow 7_{34}$	24656.04	0.11	−4.11
$8_{63} \leftarrow 8_{44}$	24642.56	0.11	−5.32
$9_{73} \leftarrow 9_{54}$	24645.68	0.06	−6.52
$10_{83} \leftarrow 10_{64}$	24682.38	−0.04	−7.69

* Transitions observed by Ferguson.

a) Experimental uncertainty in frequency measurement; ±0.05 MHz.

b) ν(calcd for rigid model) − ν(calcd for model with centrifugal distortion effect).

Table 2. Effective rotational constants, asymmetry parameter, and centrifugal distortion constants

Best fit values

A = 8614.73±0.05 MHz	d_J = −0.135 MHz
B = 8357.03±0.05 MHz	d_{JK} = 5.602 MHz
C = 4952.94±0.05 MHz	d_K = −2.30 MHz
κ = 0.859250	d_{WJ} = 1.72×10^{-5}
	d_{WK} = -6.55×10^{-4}

Corresponding values given by Ferguson[1)]

A = 8614.75±0.10 MHz
B = 8356.98±0.10 MHz
C = 4952.96±0.10 MHz
κ = 0.859213

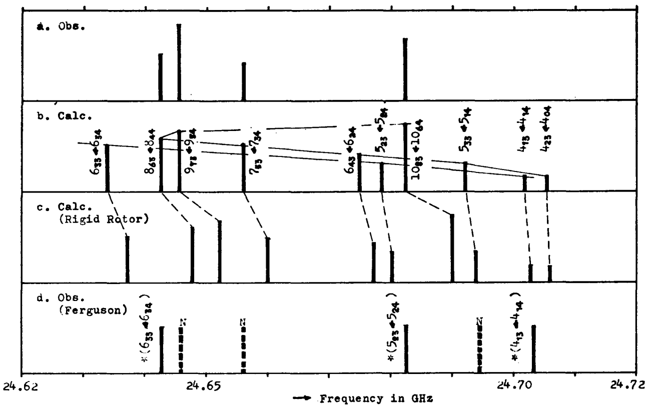

Fig. 1. Observed and calculated spectra in a range of 24.6—24.7 GHz. a. observed, b. calculated (centrifugal distortion model), c. calculated (rigid rotor model), d. observed by Ferguson.

* Assignment made by Ferguson.

N. Not assigned lines appeared in "Microwave Spectral Table", National Bureau of Standards Monograph 70, Vol. IV (1968), p. 340.

effect, (c) calculated for rigid model, and (d) observed by Ferguson are arranged in order for the region 24.6—24.7 GHz. In this region, two series of spectral lines with different sets of K_{-1} and K_{+1} overlap each other.

It is shown that, even for transitions with relatively small J values, analysis without considering the centrifugal distortion effect leads to making misassignments for molecules such as thionyl halides.[4] Clear and unequivocal assignments are given in Fig. 1.

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4) Cf. e. g., J. Burie, J. –L. Destombes, A. Dubrulle, and G. Journel, *C. R. Acad. Sci. Paris Ser. B*, **267**, 48 (1968); G. Journel, A. Dubrulle, J. –L, Destombes, and C. Marliere, *ibid.*, **271** 331 (1970).

Note added in proof. A paper by Lucas and Smith (*J. Mol. Spectrosc.*, **43**, 327 (1972)) appeared after this article had been accepted. They analysed the microwave spectrum of thionyl fluoride and obtained centrifugal distortion constants up to sextic ones. Their quartic constants, when transformed into Watson's type constants, differ from ours. It has been confirmed, however, that the constants converge to our values, if the transformed quartic constants are inserted into the least squares fit procedure we adopted (up to the quartic terms) as the initial data for iterations.