

## Extracting Vibrational Information from Rotational Spectra—A Microwave Investigation on Excited Vibrational States of SF<sub>4</sub>

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A method of extracting harmonic information from the inertial defects of non-totally symmetric vibrational states of orthorhombic molecules has been developed. As a result it has been possible to exploit additional information for a normal coordinate analysis. This information has been obtained from microwave-microwave double resonance experiments on SF<sub>4</sub> in excited vibrational states. © 1992 Academic Press, Inc.

### INTRODUCTION

Microwave rotational spectra and infrared and Raman vibration-rotation spectra depend on the values of the vibration-rotation terms of a molecule. Empirically, these terms can be expressed as the sum of a purely vibrational term, which is independent of the rotational state, and an effective rotational term, which depends slightly on the vibrational state.

The slight variation of rotational constants between different vibrational states can be determined by the analysis of the rotational spectra of excited vibrational states or by analyzing high-resolution rotation-vibration spectra.

The work of H. H. Nielsen (1) established that these changes depend on the molecular force field. Thus the experimental data are accessible and a theoretical description has been formulated, but it is, nevertheless, very difficult to use the data to derive information on the potential energy, principally because of an intermixing of quadratic and cubic force field contributions to the vibration-rotation parameters.

It is the purpose of this contribution, however, to show that in the case of non-totally symmetric vibrational states of orthorhombic molecules, it is possible to separate these otherwise intermingled contributions and thus extract purely harmonic information.

### THEORY

The vibrational dependence of the elements of the inertial tensor can be written as a series expansion in  $(v_s + d_s/2)$ , in this case truncated after the linear term,

$$I_v^{\alpha\beta} = I_e^{\alpha\beta} + \sum_s (v_s + d_s/2) \epsilon_s^{\alpha\beta}, \quad (1)$$

where the sum runs over all normal modes.  $d_s$  indicates the degeneracy of the normal mode  $s$  and  $\epsilon_s^{\alpha\beta}$  is the vibration-rotation parameter in the moment of inertia representation.

An expression for the  $\epsilon_s^{\alpha\beta}$  was first derived by H. H. Nielsen (1), and it is shown here in a slightly modified version, in which centrifugal distortion and electronic terms are omitted:

$$-\epsilon_s^{\alpha\beta} = \frac{2K}{\omega_s} \left[ -A_{ss}^{\alpha\beta} + \sum_{\gamma} \frac{a_s^{\alpha\gamma} a_s^{\beta\gamma}}{I_e^{\gamma\gamma}} + 4 \sum_r' \zeta_{sr}^{\alpha} \zeta_{sr}^{\beta} \frac{\omega_s^2}{\omega_s^2 - \omega_r^2} + \pi \sqrt{\frac{c}{h} \sum_r \frac{\Phi_{ssr} a_r^{\alpha\beta} \omega_s}{\omega_r^{3/2}}} \right]. \quad (2)$$

Here  $K = h/8\pi$ , and  $\Phi_{ssr}$  are the cubic force constants,  $\zeta_{sr}^{\alpha}$  the Coriolis coupling constants, and the  $a$  and  $A$  terms the first and second inertial derivatives,

$$\begin{aligned} a_s^{\alpha\beta} &= \partial I^{\alpha\beta} / \partial Q_s \\ A_{ss}^{\alpha\beta} &= \partial^2 I^{\alpha\beta} / \partial Q_s^2. \end{aligned} \quad (3)$$

Thus the  $\epsilon_s^{\alpha\beta}$  contain harmonic as well as anharmonic (cubic) contributions.

The terms involving the second derivatives can be eliminated using the zeta sum rule (see, e.g., Refs. (2, 3)):

$$\sum_s (\zeta_{rs}^{\alpha})^2 = A_{rr}^{\alpha\alpha} - \sum_{\gamma} (a_r^{\alpha\gamma})^2 / 4I_e^{\gamma\gamma}. \quad (4)$$

The main problem concerning the prediction (and analysis) of vibration-rotation spectra is the anharmonic part of the vibration-rotation interaction parameter  $\epsilon_s^{\alpha\beta}$ , which is more difficult to predict from a comparison of a given molecule with related ones than the harmonic contributions.

An analysis of all fundamental vibrations will yield all  $\epsilon$ 's and thus permit the calculation of equilibrium moments of inertia (and possibly the calculation of the equilibrium structure of the molecule). It is impossible, however, to separate harmonic and anharmonic contributions in the effective moments of inertia themselves. This means that it is difficult to extract purely structural information from the effective moments of inertia, and it seems equally impossible to isolate information on the *harmonic* potential.

This problem was thoroughly analyzed by Oka and Morino (3), as well as by Laurie and Herschbach (4), who came to the conclusion that although symmetry can reduce the number of cubic force constants considerably, the vibration-rotation interaction constants will always contain some anharmonicity and these contributions cannot be separated.

This is very unfortunate because the vibration-rotation parameters are some of the best sources of information on anharmonic force constants. It would therefore be reassuring to have a check on their harmonic parts in advance.

It is probably fair to state that the main purpose of the analyses in the early 1960s (3, 4) was the extraction of structural information from the "vibrationally contaminated" moments of inertia, whereas the chief target of the present study is the elucidation of the harmonic potential information contained in the inertial moments.

The conclusion of the analysis remains the same, however: The most promising path seems to be an analysis of the inertial defects.

The inertial defect is defined as:

$$\Delta^{\gamma} = I^{\gamma} - (I^{\alpha} + I^{\beta}) \quad (5)$$

where the  $\gamma$ -direction is taken as perpendicular to the  $\alpha\beta$ -plane.

It can be shown that when  $I^{\gamma}$  represents (as usual) the largest and  $I^{\alpha}$  the smallest principal moment of inertia, then the *structurally* defined inertial defect,  $\Delta^{\gamma}$ , must be

zero for a planar, rigid molecule. By examining the effective moments of inertia of the water molecule R. Mecke (5) realized, however, that the relationship

$$I^{cc} = I^{aa} + I^{bb} \quad (6)$$

was violated. The deviation  $I^{cc} - (I^{aa} + I^{bb})$  was later termed inertial defect. Although the meaning of "inertial defect" only truly characterizes the relationship of inertial moments in planar molecules, where it can be described as the discrepancy between the measured (effective) and structurally defined linear combination (Eq. (6)) of inertial moments, this term is generally used to describe the parameter defined by Eq. (5) for all molecules.

A theoretical analysis by Darling and Dennison (6) showed that this parameter is purely harmonic for planar molecules.

Under neglect of centrifugal distortion and electronic as well as off-diagonal contributions, the vibrational contribution to the inertial defect of the ground state or an excited vibrational state can be written as

$$\Delta_v^\gamma = \sum_s (v_s + d_s/2)(\epsilon_s^{\gamma\gamma} - \epsilon_s^{\alpha\alpha} - \epsilon_s^{\beta\beta}). \quad (7)$$

Normally, the inertial defect will contain anharmonic as well as harmonic contributions, but for planar molecules

$$\Delta^\gamma(\text{anharm}) = \sum_s (a_s^{\gamma\gamma} - a_s^{\alpha\alpha} - a_s^{\beta\beta}) \langle Q_s \rangle = 0 \quad (8)$$

because  $a_s^{\gamma\gamma} = a_s^{\alpha\alpha} + a_s^{\beta\beta}$  for all  $s$ , and all anharmonic terms disappear.

This relationship is valid only for planar molecules. There exists, however, one more class of molecules from which it is possible to extract the purely harmonic contribution to the inertial defect, at least for non-totally symmetric vibrational states: orthorombic molecules (Point groups  $D_{2h}$ ,  $D_2$ , and  $C_{2v}$ ), regardless of planarity.

The reason for this fact must be searched for (and is found) in the first inertial derivative matrix  $a$ . Group theoretical considerations show that the elements  $a_s^{\alpha\beta}$  are nonvanishing only in the case of  $\Gamma(\hat{J}_\alpha) \times \Gamma(\hat{J}_\beta) \supset \Gamma(Q_s)$ ; i.e., the irreducible representation of the normal coordinate must be contained in the direct product of the rotational species involved.

Let us take a closer look at the inertial tensor in the vibrational ground state and in an excited vibrational state in order to elucidate this group theoretical statement.

The inertial tensor in the principal axis system of the ground state is

$$\begin{Bmatrix} I_\circ^{\alpha\alpha} & 0 & 0 \\ 0 & I_\circ^{\beta\beta} & 0 \\ 0 & 0 & I_\circ^{\gamma\gamma} \end{Bmatrix}. \quad (9)$$

All terms contain harmonic and anharmonic contributions according to Eq. (1).

The inertial defect is

$$\Delta_\circ^\gamma = I_\circ^{\gamma\gamma} - I_\circ^{\alpha\alpha} - I_\circ^{\beta\beta}. \quad (10)$$

The inertial tensor is changed upon excitation of the  $s$ th normal vibration. The changes are the  $\epsilon$ 's that have already been introduced in Eq. (2).

Now, in order to evaluate these changes, one must know the structure of the  $A$ -,  $a$ -, and  $\zeta$ -matrices. These elements can all be calculated from a harmonic force field

TABLE I  
 $a$ -Matrix (First Inertial Derivatives) for  $SF_4$

	aa	bb	cc	ab	bc	ac
$v_1$	14.251	7.551	9.613	0	0	0
$v_2$	-1.123	16.137	20.602	0	0	0
$v_3$	9.593	-3.638	10.008	0	0	0
$v_4$	-2.327	-12.800	-3.241	0	0	0
$v_5$	0	0	0	11.920	0	0
$v_6$	0	0	0	0	0	2.033
$v_7$	0	0	0	0	0	8.114
$v_8$	0	0	0	0	-7.152	0
$v_9$	0	0	0	0	3.104	0

alone. In order to recall what they typically look like, these matrices have been listed in Tables I, II, and III for  $SF_4$  (calculated with the normal coordinate program NCA (7)).

The inertial tensor of an excited vibrational state will take one of the following forms for totally symmetric and non-totally symmetric vibrational states:

(1) For totally symmetric vibrations: Due to the contributions from  $A$ -,  $a$ -, and  $\zeta$ -terms, harmonic as well as anharmonic elements are added to the diagonal elements (contributions to the moments of inertia). No off-diagonal elements (contributions to the products of inertia) appear, but harmonic and anharmonic contributions in the diagonal elements are inseparable.

(2) For non-totally symmetric vibrations: Due to the contributions from  $A$ - and  $\zeta$ -terms, harmonic elements are added to the diagonal terms. For each vibration at most one off-diagonal element (anharmonic) is added. This is *characteristic* and *unique* for orthorhombic molecules.

Indicating the nonvanishing off-diagonal element with  $\alpha\beta$ , the inertial tensor of the non-totally symmetric excited vibrational state will take the form

$$\begin{Bmatrix} I_{\circ}^{\alpha\alpha} + H^{\alpha\alpha} & A^{\alpha\beta} & 0 \\ A^{\alpha\beta} & I_{\circ}^{\beta\beta} + H^{\beta\beta} & 0 \\ 0 & 0 & I_{\circ}^{\gamma\gamma} + H^{\gamma\gamma} \end{Bmatrix}, \quad (11)$$

TABLE II

$A$ -Matrix (Second Inertial Derivatives) for  $SF_4$  aa, bb, etc. Indicate the Elements in Relation to the Principal Axes

	aa	bb	cc	ab	bc	ac
$v_1$	0.995	0.694	0.311	0	0	0
$v_2$	0.126	0.987	0.887	0	0	0
$v_3$	0.994	0.397	0.627	0	0	0
$v_4$	0.885	0.940	0.175	0	0	0
$v_5$	0.346	0.654	1.000	0	0	0
$v_6$	0.010	1.000	0.990	0	0	0
$v_7$	0.161	1.000	0.839	0	0	0
$v_8$	1.000	0.235	0.765	0	0	0
$v_9$	1.000	0.044	0.956	0	0	0

TABLE III  
 $\zeta$ -Matrix for SF<sub>4</sub>

$\zeta^a$	1	2	3	4	5	6	7	8	9
1	0	0	0	0	0	0	0	-0.447	-0.350
2	0	0	0	0	0	0	0	0.234	-0.259
3	0	0	0	0	0	0	0	0.781	0.282
4	0	0	0	0	0	0	0	0.369	-0.855
5	0	0	0	0	0	0.059	0.236	0	0
6	0	0	0	0	-0.059	0	0	0	0
7	0	0	0	0	-0.236	0	0	0	0
8	0.447	-0.234	-0.781	-0.369	0	0	0	0	0
9	0.350	0.259	-0.282	0.855	0	0	0	0	0

  

$\zeta^b$									
1	0	0	0	0	0	-0.623	-0.436	0	0
2	0	0	0	0	0	0.021	0.678	0	0
3	0	0	0	0	0	0.593	0.025	0	0
4	0	0	0	0	0	-0.509	0.591	0	0
5	0	0	0	0	0	0	0	0.392	-0.170
6	0.623	-0.021	-0.593	0.509	0	0	0	0	0
7	0.436	-0.678	-0.025	-0.591	0	0	0	0	0
8	0	0	0	0	-0.392	0	0	0	0
9	0	0	0	0	0.170	0	0	0	0

  

$\zeta^c$									
1	0	0	0	0	0.405	0	0	0	0
2	0	0	0	0	-0.459	0	0	0	0
3	0	0	0	0	0.684	0	0	0	0
4	0	0	0	0	0.398	0	0	0	0
5	-0.405	0.459	-0.684	-0.398	0	0	0	0	0
6	0	0	0	0	0	0	0	-0.559	-0.815
7	0	0	0	0	0	0	0	-0.591	0.522
8	0	0	0	0	0	0.559	0.591	0	0
9	0	0	0	0	0	0.815	-0.522	0	0

where  $H$  and  $A$  indicate "harmonic" and "anharmonic" contributions. The  $\gamma$ -axis is chosen as the direction perpendicular to the  $\alpha\beta$ -plane containing the nonvanishing off-diagonal element.

In order to calculate the inertial moments and the inertial defect of the excited state, this tensor must be diagonalized, however. Diagonalization is a unitary transformation which leaves the trace invariant, and since there are no off-diagonal elements connecting  $I^{\gamma\gamma}$  with  $I^{\alpha\alpha}$  and  $I^{\beta\beta}$ , the sum of  $I^{\alpha\alpha}$  and  $I^{\beta\beta}$  remains *unchanged* after the transformation.

Consequently, the inertial defect of the excited state can be written as

$$\Delta_s^\gamma = I_s^{\gamma\gamma} + H^{\gamma\gamma} - (I_s^{\alpha\alpha} + H^{\alpha\alpha} + I_s^{\beta\beta} + H^{\beta\beta}) \quad (12)$$

and the difference to the ground state given in Eq. (10) as

$$\Delta\Delta_s^\gamma \equiv \Delta_s^\gamma - \Delta_0^\gamma = H^{\gamma\gamma} - (H^{\alpha\alpha} + H^{\beta\beta}), \quad (13)$$

i.e., the *inertial defect difference* between the ground state and a non-totally symmetric vibrational state of an orthorhombic molecule is a purely harmonic piece of information that can be exploited in a normal coordinate analysis. Because the centrifugal distortion and electronic terms normally hardly vary between the ground state and excited vibrational states, these terms can safely be neglected due to the subtraction involved in the calculation of the inertial defect differences.

Since  $\gamma$  can be chosen freely (the choice depending only on the nonvanishing off-diagonal element for a particular vibration) all non-totally symmetric vibrations will contribute harmonic information.

Simultaneously, for these vibrations one obtains the best possible check on the harmonic part of the vibration-rotation parameters.

One further point about the inertial defect differences must be emphasized in order to explain their usefulness in a normal coordinate analysis: The derivatives of inertial defect differences with respect to internal coordinate force constants are much stronger contributors to the Jacobian matrix than are isotopic shifts or centrifugal distortion constants—not to mention vibrational amplitudes (see Table VIII). They are prone to large changes upon minor variations of the force field, though, and may be difficult to include at the beginning of a normal coordinate analysis, when the final assignment has not yet been established.

#### EXPERIMENTAL CONSIDERATIONS

The microwave spectrum of  $\text{SF}_4$  in the ground state was first recorded by Tolles and Gwinn (8). Later, Hirota and co-workers analyzed two vibrationally excited states ( $\nu_4$  and  $\nu_9$ ) (9) in order to settle a dispute among vibrational spectroscopists regarding the assignment of the vibrational spectrum (10, 11). The main dispute concerned the energy of the two lowest-lying vibrational states, a matter that could be unravelled through the determination of the vibrational satellite intensities in the microwave spectrum. The final assignment of the complete vibrational spectrum, however, was not reached at that time. Consequently, matrix isolation spectra were recorded in order to establish the  $^{32}\text{S}$ – $^{34}\text{S}$  isotopic shifts with high precision and to incorporate these measurements in the normal coordinate analysis (12). This assignment of the normal vibrations and their isotopic shifts is shown in Table IV, and the derived symmetry force field is shown in Table V.

This result, however, cannot represent the final vibrational analysis of  $\text{SF}_4$ .

First, the information on the  $A_1$ -part of the force field is insufficient to determine all parameters. Second, the infrared inactive  $\nu_5$ -vibration has never been observed. In Ref. (12)  $F_{55} \approx F_{77}$  was assumed and thus  $\nu_5$  was estimated to be  $\sim 437 \text{ cm}^{-1}$ . This is the point where microwave spectroscopy can once more yield additional information.

TABLE IV  
Fundamental Vibrations and  $^{34}\text{S}$ – $^{32}\text{S}$  Isotopic Shifts in a Ne Matrix ( $\text{cm}^{-1}$ )

Sym	Vibration	Frequency <sup>a</sup>	Isotopic shift <sup>a</sup>
$A_1$	$\nu_1$	892	11.33
	$\nu_2$	558	0.
	$\nu_3$	532	4.09
	$\nu_4$	228	–
$A_2$	$\nu_5$	[437]	–
$B_1$	$\nu_6$	730	13.13
	$\nu_7$	475	–
$B_2$	$\nu_8$	867	10.52
	$\nu_9$	353	2.42

<sup>a</sup> Ref. (12).

TABLE V  
Symmetry Force Field for SF<sub>4</sub> (Ref. (12))

F <sub>11</sub> =	5.884	F <sub>12</sub> =	0	F <sub>13</sub> =	0.320	F <sub>14</sub> =	0.300
F <sub>22</sub> =	3.476	F <sub>23</sub> =	0.10	F <sub>24</sub> =	0		
F <sub>33</sub> =	1.414	F <sub>34</sub> =	0.4913				
F <sub>44</sub> =	0.863						
F <sub>55</sub> =	[1.673]						
F <sub>66</sub> =	2.821	F <sub>67</sub> =	0.530				
F <sub>77</sub> =	1.673						
F <sub>88</sub> =	5.165	F <sub>89</sub> =	0.700				
F <sub>99</sub> =	1.914						

Note. Force constants in N/cm. Deformations normalized on 10<sup>-8</sup> cm.

Relative intensity measurements on vibrational satellites normally yield vibrational frequencies with an estimated accuracy of  $\sim 10\%$ . Such estimates will not improve the cited normal coordinate analysis. But SF<sub>4</sub> is an orthorhombic molecule (point group  $C_{2v}$ ), and therefore inertial defect differences, which can be measured with very high precision, could provide additional useful information on the force field.

The analysis of vibrational satellites of rotational transitions is complicated by the fact that the intrinsically weak lines can originate from various excited states, the rotational constants of which do not differ strongly from the rotational constants of the ground state. The assignment, therefore, is not always straightforward.

One escape from this dilemma is the use of the strongly selective double resonance technique, where signals are only recorded provided both radiation frequencies match a molecular three-level system. Thus one level in this system must be common to both (pump- and signal-) transitions.

The MW-MW DR spectrum of SF<sub>4</sub> was obtained with a crossed Fabry-Perot interferometer double resonance cell, allowing for pump frequencies in the *K*-band (18–26.4 GHz) and signal frequencies in the *Ka* band (26.4–40 GHz) (13).

In these frequency ranges only a few DR signals occur, but because of the above-mentioned DR requirements, a few DR signals suffice for an unequivocal assignment.

The pump frequency was optimized to produce a symmetrical signal form (for a discussion of MW-MW DR line shapes, see, e.g., Ref. (14)). This optimization allows only an accuracy of the magnitude of 1 MHz for the pump frequency, whereas the signal frequency is determined with an accuracy of  $\sim 100$  kHz. Therefore, the measured frequencies of the ground state as well as the  $\nu_4$ - and  $\nu_9$ -states are compared with the Stark effect modulated measurements of Refs. (8, 9). The newly found transitions ( $\nu_5$  and  $\nu_7$  states) were assigned according to relative intensities (Boltzmann distribution and spin statistics). The frequencies of the measured DR signals are shown in Table VI.

The derived rotational constants (as well as the inertial defects and the inertial defect differences) are to be found in Table VII.

In order to decide which inertial defect differences are relevant to the normal coordinate analysis, the  $A$ -,  $a$ -, and  $\zeta$ -matrices must be analyzed (Tables I, II, and III).

Obviously no harmonic information can be extracted from the inertial defect difference of the totally symmetric vibration  $\nu_4$ , but only for the non-totally symmetric vibrations  $\nu_5$ ,  $\nu_7$ , and  $\nu_9$ .

TABLE VI

Measured Microwave-Microwave Double Resonance Transitions (Pump- and Signal-) in SF<sub>4</sub> (MHz)

$v$	$v = 0$	$v_4$	$v_5$	$v_7$	$v_9$
1 <sub>10</sub> 2 <sub>20</sub>	23466.00	23331.60	23442.00	23444.40	23518.80
a)	23466.10	23331.03			23518.94
2 <sub>20</sub> 3 <sub>30</sub>	37038.00	36807.27	37005.60	37012.39	37133.03
1 <sub>11</sub> 2 <sub>21</sub>	24150.75	24021.25	24128.75	24108.75	24198.75
a)	24149.76	24020.93			24199.16
2 <sub>21</sub> 3 <sub>31</sub>	37195.95	36792.60	37164.56	37158.98	37287.15
2 <sub>02</sub> 3 <sub>12</sub>	27608.24	27615.80	27560.08		27570.16
a)	27608.05	27617.46			27568.64
3 <sub>12</sub> 4 <sub>22</sub>	38061.75	37984.98	37996.30		38061.59

<sup>a</sup> Refs. (8) and (9), respectively.

Table II shows clearly that in  $v_5$  the anharmonic off-diagonal element is an *ab*-element, whereas the relevant elements in  $v_7$  and  $v_9$  are *ac*- and *bc*-elements, respectively.

Thus the relevant inertial defect differences for the normal coordinate analysis are  $\Delta\Delta_5^c$ ,  $\Delta\Delta_7^b$ , and  $\Delta\Delta_9^a$ .

The following information is available for a normal coordinate analysis:

8 frequencies (fundamental vibrations)

3 centrifugal distortion constants

5 vibrational amplitudes (from the electron diffraction analysis (15))

6 isotopic shifts

and

3 inertial defect differences.

The general valence force field consists of 22 force constants of which only 17 are linearly independent (because of symmetry).

Technically, sufficient information is therefore available for a complete normal coordinate analysis, but some of the data do not contribute significantly to the Jacobian matrix (see Table VIII).

TABLE VII

Rotational Constants (MHz), Inertial Defects, and Inertial Defect Differences ( $\mu \text{ \AA}^2$ ) for SF<sub>4</sub>

	$v = 0$	$v_4$	$v_5$	$v_7$	$v_9$
A	6687.762	6641.663	6683.547	6685.06	6707.702
B	4086.652	4095.612	4077.446	4053.59	4076.104
C	3219.497	3214.616	3206.810	3220.90	3217.644
$\Delta^a$	-205.0709	-204.5142	-205.9235	-205.9808	-205.7060
$\Delta^b$	-108.8756	-109.9090	-109.2651	-107.8291	-108.4214
$\Delta^c$	-42.2587	-42.2743	-41.9645	-43.3662	-42.2636
$\Delta\Delta^a$		0.5567	-0.8526	-0.9098	-0.6351
$\Delta\Delta^b$		-1.0334	-0.3895	1.0465	0.4542
$\Delta\Delta^c$		-0.0156	0.2942	-1.1075	-0.0049

TABLE VIII  
Jacobian Matrix for SF<sub>4</sub>

f <sub>ij</sub>	SF <sub>ax</sub>	SF <sub>eq</sub>	FSF <sub>ax</sub>	FSF <sub>eq</sub>	F <sub>ax</sub>	SF <sub>eq</sub>	R/R	r/r	R/r	r/r	r/α	R/α	R/β	R/γ	α/β
	R	r	γ	β	α										
v <sub>4</sub>	16.2	0.9	110.4	36.2	40.3		16.2	0.9	15.5	17.3	72.3	-69	-29	-152.9	
v <sub>9</sub>	0	0	0	0	92.4		0	0	0	-2.1	0	0	0	0	0
Δv <sub>1</sub>	0	-0.3	-2.2	-1.6	-1.0		0	-0.3	-0.1	3.7	0.4	0.6	-0.6	-5.0	
τ <sub>aaaa</sub>	0.1	1.5	3.4	0	1.4		0.1	1.5	-1.4	4.1	0.9	-6.5	-1.4	0.4	
l <sub>14</sub>	0	-0.2	0	0	0		0	0	0	0.1	0	0	0	0	
ΔΔ <sub>5</sub> <sup>C</sup>	16.4	-7.5	-61.5	-37.0	90.7		-56	-8.5	-98.1	-45	593	76.4	-98	-127.7	

Note.  $\nu$ : harmonic frequencies;  $\Delta\nu$ : isotopic shifts;  $\tau$ : centrifugal distortion;  $l$ : vibrational amplitudes;  $\Delta\Delta$ : inertial defect differences.

Nevertheless, the results of the normal coordinate treatment have been collected in the Tables IX, X, and XI.

Table IX shows the comparison between experimental and calculated data. Table X shows the derived general valence force field and Table XI the resulting symmetry force field for a comparison with Table V, in which the U-matrix of Ref. (10) has been used.

Two points of interest are worth emphasizing:  $\nu_5$  is now calculated at 470 cm<sup>-1</sup>, whereas a position of 437 cm<sup>-1</sup> was estimated in Ref. (12). The symmetry force constant  $F_{55}$  accidentally equals  $F_{99}$  and is larger than  $F_{77}$ .

It is obvious that the  $B_1$ - and  $B_2$ -blocks have hardly changed upon incorporating this new information, but the  $A_1$ -block shows some changes, perhaps introduced through the determination of some general valence force field interaction constants.

The potential energy distribution shows that a description of  $\nu_4$  as *axial deformation* and  $\nu_3$  consequently as *equatorial deformation* now bears more weight than in Ref. (12).

TABLE IX  
Measured and Calculated Data for the Normal Coordinate Analysis of SF<sub>4</sub>

	Measured	Calculated	Measured	Calculated
v <sub>1</sub>	892	892.3	Δv <sub>1</sub>	-11.33
v <sub>2</sub>	558	556.2	Δv <sub>2</sub>	0
v <sub>3</sub>	532	530.2	Δv <sub>3</sub>	-4.09
v <sub>4</sub>	228	227.8	Δv <sub>4</sub>	-
v <sub>5</sub>	-	470.1	Δv <sub>5</sub>	-
v <sub>6</sub>	730	729.4	Δv <sub>6</sub>	-13.13
v <sub>7</sub>	475	476.9	Δv <sub>7</sub>	-
v <sub>8</sub>	867	866.8	Δv <sub>8</sub>	-10.52
v <sub>9</sub>	353	354.4	Δv <sub>9</sub>	-2.40
τ <sub>aaaa</sub>	-0.0152	-0.0122	l <sub>SF<sub>eq</sub></sub>	0.041
τ <sub>bbbb</sub>	-0.0078	-0.0102	l <sub>SF<sub>ax</sub></sub>	0.047
τ <sub>cccc</sub>	-0.0049	-0.0019	l <sub>FF<sub>eq</sub></sub>	0.068
ΔΔ <sub>5</sub> <sup>C</sup>	0.2942	0.2911	l <sub>FF<sub>eq</sub></sub>	0.067
ΔΔ <sub>5</sub> <sup>B</sup>	1.0465	1.0434	l <sub>FF<sub>ax</sub></sub>	0.074
ΔΔ <sub>5</sub> <sup>A</sup>	-0.6351	-0.6357		0.071

Note: Vibrational frequencies ( $\nu$ ) and isotopic shifts ( $\Delta\nu$ ) in cm<sup>-1</sup>, centrifugal distortion constants ( $\tau$ ) in MHz, and inertial defect differences ( $\Delta\Delta$ ) in u Å<sup>2</sup>. Vibrational amplitudes in Å.

TABLE X  
General Harmonic Force Field for  $\text{SF}_4$

$\text{SF}_{\text{ax}}$ (R)	3.022	$\text{R}/\alpha$	-0.200	$\beta/\gamma$	-0.363
$\text{SF}_{\text{eq}}$ (r)	5.475	$\text{r}/\alpha$	0.027	$\alpha/\beta$	-0.054
$\text{FSF}_{\text{ax}}$ ( $\gamma$ )	1.192	$\text{R}/\alpha'$	-0.571	$\alpha/\gamma$	0.144
$\text{FSF}_{\text{eq}}$ ( $\beta$ )	1.942	$\text{r}/\alpha'$	-0.463	$\alpha/\alpha'$	-0.264
$\text{FaSF}_{\text{e}}$ ( $\alpha$ )	1.550	$\text{R}/\beta$	0.488	$\alpha/\alpha'$	-0.264
$\text{R}/\text{R}$	0.217	$\text{r}/\beta$	0.532	$\alpha/\alpha''$	-0.385
$\text{r}/\text{r}$	0.316	$\text{R}/\gamma$	-0.014		
$\text{R}/\text{r}$	0.104	$\text{r}/\gamma$	-0.233		

*Note.* Dimensions as in Table V.

### DISCUSSION

Rotational and vibrational spectroscopy are of course fundamentally interconnected, and especially the analysis of the rotational fine structure of vibration-rotation bands has in numerous cases led to the determination of rotation-vibration parameters.

As this contribution shows, in some cases it is also possible to analyze the "vibrational fine structure" of rotational spectra (of molecules in thermally populated vibrational states) not only to obtain information about the rotation-vibration parameters but also to acquire purely potential information without relinquishing the intrinsic high accuracy of microwave spectroscopy.

A look at Table IX shows that the inertial defect differences in this case have been very well fitted. It is as yet uncertain, though, whether weak Coriolis or anharmonic interaction, which normally would not show up in the analysis of the rotational spectra, because the small deviations from a rigid rotor model are being absorbed in the ordinary rotational and centrifugal distortion constants, will in fact influence the measured inertial defect differences.

In order to gain more insight on this particular problem and to obtain more experience in using this new method of analysis in general, a reinvestigation of some difluoroethylenes is planned for the near future (16).

TABLE XI  
Symmetry Force Field for  $\text{SF}_4$

$\text{F}_{11}$	5.791	$\text{F}_{12}$	0.208	$\text{F}_{13}$	0.779	$\text{F}_{14}$	0.043
$\text{F}_{22}$	3.239	$\text{F}_{23}$	0.729	$\text{F}_{24}$	0.480		
$\text{F}_{33}$	1.957	$\text{F}_{34}$	-0.223				
$\text{F}_{44}$	0.553						
$\text{F}_{55}$	1.935						
$\text{F}_{66}$	2.805	$\text{F}_{67}$	0.529				
$\text{F}_{77}$	1.693						
$\text{F}_{88}$	5.159	$\text{F}_{89}$	0.693				
$\text{F}_{99}$	1.935						

*Note.* Dimensions as in Table V.

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