Vol. A51 (1977) ACTA PHYSICA POLONICA No 5

VIBRATIONAL ANALYSIS OF TRIFLUOROAMINE OXIDE*

By G. Shanmugam

Department of Crystallography and Biophysics, University of Madras**

(Received December 30, 1975; revised version received October 28, 1976)

Green's function has been applied to the vibrational analysis of trifluoroamine oxide (ONF_3). This approach has been found to yield a reliable set of force constants. Mean amplitudes of vibration were calculated to supplement the force field study.

1. Introduction

Trifluoroamine oxide (ONF_3) was first synthetized in 1966 [1, 2] and the earliest infrared spectra were reported subsequently [3, 4]. There were some discrepancies in assigning the ν_3 and ν_5 modes. The assignment made by Hirschmann et al. [5], described the band at 528 cm^{-1} to the ν_3 mode and 558 cm^{-1} to the ν_5 mode, reversing the earlier assignments. To supplement their assignment they recorded the IR spectrum of the isotopically pure $O^{15}NF_3$ and made a normal coordinate treatment. They obtained a non-negative NO–NF interaction constant only for the above values (and they obtained negative values of interaction constant when they assumed a degeneracy between ν_3 and ν_5; and when $\nu_3 = 558$ and $\nu_5 = 528$ cm^{-1}). Abramowitz and Levin [6] reported the Raman spectra of thin film of ONF_3 condensed at liquid nitrogen temperature. Normal coordinate analysis made by these workers support a value of 513 cm^{-1} for the ν_5 mode. Then in 1973, Barney and Cormier [7] gave a vibrational assingment for both $O^{14}NF_3$, and $O^{15}NF_3$, and a normal coordinate analysis employing a UBFF. They assigned the ν_3 mode at 528 cm^{-1} and ν_5 at 513 cm^{-1}. Subsequently, the Raman spectrum of the gaseous ONF_3 was reported by Aminadav et al. [8]. They assigned the ν_3 mode at 542 cm^{-1} and the ν_5 mode at 528 cm^{-1}. Recently these assignments have been again reversed by Christe et al. [9]. They assigned 542 cm^{-1} for the ν_3 mode and 529 cm^{-1} for the ν_5 mode. These assignments have been well established by the polarization data. However these recent data do not supplement isotopic data, essential for Green's function analysis, which is the main aim

* Contribution No. 443 from the Department.

** Address: Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras-600025, India.

of the present study. So the present work makes use of the IR data (Table I) given by Berney and Cormier [7] for $O^{14}NF_3$ and $O^{15}NF_3$. The geometry assumed in this work is that given by Plato et al. [10] from electron diffraction study.

TABLE I

Molecular parameters of ONF_3

Vibrational mode	Frequency [7] in cm^{-1}		Geometry [10]
	$O^{14}NF_3$	$O^{15}NF_3$	
a_1 species: ν_1	1689	1657	$R_{N-O} = 1.159$ Å
ν^2	740	734	$r_{N-F} = 1.432$ Å
ν_3	528	526	$\alpha = \sphericalangle FNF = 100.5°$
e species: ν_4	880	859	$\beta = \sphericalangle FNO = 117.4°$
ν_5	513	513	
ν_6	398	396	

The results obtained do favour the assignment used. The NO–NF interaction constant is postive. Further, supporting evidence is made by calculating the mean amplitudes of vibration for the NO and NF bonds.

2. Symmetry and point group

NMR data for ONF_3 indicate [1, 2] that the three fluorine atoms are equivalent and the molecule belongs to the C_3v point group. The nine fundamental modes of vibrations are: the three a_1 type vibrations which include the NO stretch, the totally symmetric NF stretch and the symmetric FNF angle deformation; and the doubly degenerate e type vibration includes the asymmetric NF stretch, the asymmetric FNF, and FNO angle deformations. Normal coordinate treatment of this type of molecules were made by Ziomek and Piotrowski [11]. The internal symmetry coordinates, the inverse kinetic energy matrices obtained and potential energy matrices used in determinig the valence force constants are essentialy the same as the ones reported by them. The internal symmetry coordinates (U) and the potential energy matrices (F) were also given by Hirschmann et al. [5]. However there is one typographical error in their F_{46} element. The correct expression is, $F_{46} = d(f'_{d\alpha} - f_{d\alpha})$ and not $d^2(f'_{d\alpha} - f_{d\alpha})$ as given by Hirschmann et al.

3. Green's function for Y_3XZ molecule

The six translational and rotational coordinates were constructed by the method suggested by Meal and Polo [12]. The nine vibrational (external) symmetry coordinates (S) were constructed following the group theoretical methods suggested by Bhagavantham [13]. These $3n$ coordinates (three translational, three rotational and nine vibrational) transform according to the irreducible representation of the C_3v point group. Further the conditions namely $UDS = B$ and $B\tilde{B} = G$, the inverse kinetic energy matrix are obeyed.

Here, D is the transformation matrix between internal and cartesian coordinates. Once the external symmetry coordinates are constructed, the normal coordinates can be written as linear combinations of the symmetry coordinates [14–17, 20]. Like the symmetry coordinates, the normal coordinates are also normalized, and made orthogonal to each other and found to transform according to the irreducible representation of the point group of the molecule. (Here the normal coordinates actually represent each normal mode of vibration).

Eventhough the normal coordinates are column vectors having $3n$ (n is the number of atoms) elements, it is sufficient if the elements cooresponding to the perturbed atom alone are considered. (The three rows of the x, y and z coordinates of the atom). A perturbation associated with those three rows, namely [20],

$$G_{ij}(\omega^2) = \sum_k Q_{ik}Q_{jk}/(\omega^2-\omega_k 2) \tag{1}$$

gives Green's function for the molecule[1]. The Green function elements obtained from the x and y coordinates, $G_{11}(\omega^2)$ and $G_{22}(\omega^2)$ are equal, which correspond to the doubly degenerate species. The Green function element obtained from the Z coordinates corresponds to the a_1 species. All other $G_{ij}(\omega^2)$ terms are zero. They are given below

$$G_{11}(\omega^2) = G_{22}(\omega^2) = \frac{Q_{x4}^2}{\omega^2-\omega_4^2} + \frac{Q_{x5}^2}{\omega^2-\omega_5^2} + \frac{Q_{x6}^2}{\omega^2-\omega_6^2} + \frac{p^2 m_x}{I_x} + \frac{m_x}{M}$$

$$G_{33}(\omega^2) = \frac{Q_{Z1}^2}{\omega^2-\omega_1^2} + \frac{Q_{Z2}^2}{\omega^2-\omega_2^2} + \frac{Q_{Z3}^2}{\omega^2-\omega_3^2} + \frac{m_x}{M} \tag{2}$$

and $G_{12}(\omega^2) = G_{21}(\omega^2)$; $G_{13}(\omega^2) = G_{31}(\omega^2)$; $G_{23}(\omega^2) = G_{32}(\omega^2)$ and all are equal to zero. The terms occuring in the $Gij(\omega^2)$ values are defined in the appendix. By substituting the above $G_{ij}(\omega^2)$ values in the determinantal equation [14, 20], we get a 3×3 determinant, block diagonalized according to the C_3v symmetry, $3a_1+3e$. We get,

$$[\varepsilon\omega^2 G_{11}(\omega^2)+1] = 0, \quad [\varepsilon\omega^2 G_{22}(\omega^2)+1] = 0$$

and

$$[\varepsilon\omega^2 G_{33}(\omega^2)+1] = 0. \quad \text{Here} \quad \varepsilon = (m_x^i - m_x)/m_x.$$

The roots of the above first two equations correspond to the frequencies of the e species and that of the third one correspond to the frequencies of the a_1 species, containing the isotopic sum and product rules.

4. Force constants and mean amplitudes of vibration

By substituting the frequencies of the natural and isotopic molecules in the isotopic rules, the mixing parameters are determined. Using them, the mixing parameter matrix is constructed and in the usual way of the force constants are determined [17, 20].

[1] In Q_{ik} and Q_{jk}, subscript k refers to the normal mode. i and j have values in three cartesian coordinate systems namely in x, y and z coordinates.

TABLE II

Force constants of ONF_3

Symmetry force constants	Valence force constants		
		Present work	Hirschmann et al. [5]
a_1 species			
F_{11} = 13.8858	f_R	13.8858	11.64
F_{22} = 4.8490	f_r	4.3478	4.25
F_{33} = 1.2490	f_α	0.9358	1.3
F_{12} = 1.3755	f_β	1.0442	1.23
F_{13} = −0.8090	f_{Rr}	0.7941	0.24
F_{23} = 0.7374	$f_{R\alpha}$	−0.3302	0.09
e species	$f_{R\beta}$	0.3302	0.20
F_{44} = 4.0973	f_{rr}	0.2505	0.38
F_{55} = 1.0916	$f_{r\alpha}$	0.2824	0.62
F_{66} = 1.2542	$f'_{r\alpha}$	−0.0434	−0.20
F_{45} = −0.3259	$f_{r\beta}$	−0.7069	0.39
F_{46} = −0.7997	$f'_{r\beta}$	0.0927	−0.20
F_{56} = 0.3000	$f_{\alpha\beta}$	−0.1081	—
	$f'_{\alpha\beta}$	−0.4081	—
	$f_{\beta\beta}$	−0.2098	—

Stretching and stretch: stretch constants are expressed in md/Å; bond angle interaction: md/r; angle bend and angle-angle interaction: md A/r^2. The prime notation corresponds to either a bond-opposite angle or an angle-opposite angle interaction.

TABLE III

Root mean square vibrational amplitudes of ONF_3 in Å

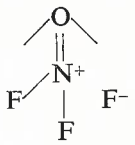
$\sigma_{element}$	Present work	Electron diffraction value [10]
σ_{N-O}	0.035	0.029
σ_{N-F}	0.058	0.051

To supplement the force constants obtained, the mean amplitudes of vibration are calculated as suggested by Cyvin [18] and these values are given in Table III along with the electron diffraction results of Plato et al. [10].

5. *Results and discussion*

The symmetry force constant matrix and the valence force constants obtained therefrom are presented in Table II. Regarding the off diagonal elements of the F matrix, they are comparatively much smaller than diagonal terms, a general feature expected in the force field study. The N−O bond stretching force constant obtained is 13.88 m dyn/Å, which

is slightly higher than the value given by Hirschmann et al. (11.64 mdyn/Å). However, this value is comparable with the value of 13.59 mdyn/Å obtained by Ramaswamy and Mohan [19] for the same molecule, but through a different approach. Further this value (13.88 mdyn/Å for a bond length = 1.159 Å) is consistant with the value obtained by us (10.67 mdyn/Å for the bond length of 1.97 Å) for the NO_2 molecule [20]. This value obtained, indicates a bond order of approximately two. This double bond character is explained on the basis of the resonance structure by Christe et al.According to them the resonance structure is shown below



The three N—F bonds are highly polar implying a very strong contributions from the resonance structure. The occurance of this type of bonding can be rationalized by the high electronegativity of the fluorine atom.

The N—F stretching constant obtained is 4.35 mdyn/Å. The corresponding value obtained by Hirschmann et al. is 4.25 mdyn/Å while Ramaswamy and Mohan reported a value of 4.53 mdyn/Å. The FNF angle bending force constant is 0.94 mdyn/r^2 while Hirschmann et al. report a value of 1.3 mdyn/r^2. Here 1.04 mdyn/r^2 is obtained for the FNO angle bending while the value reportd by them is 1.23 mdy/r^2. As claimed by Hirschmann et al. a non-negative value is also obtained here for the NO–NF interaction constant (= 0.79 mdyn/Å). Another interesting feature of the results is the values obtained for $f_{R\alpha}$ and $f_{R\beta}$; they are respectively −0.33 and 0.33 mdyn/radian, having equal magnitude and opposite directions. The other valence constants obtained are also given in the Table.

As said already, to supplement the force constants obtained, the mean amplitudes of vibration for the two bonded atom pairs are calculated. They are, σN—O = 0.035 Å and σN—F = 0.058 Å which compare well with the electron diffraction values, justifying the force constants obtained. These results reveal that the Green function is applicable to this molecule in order to arrive at an exact set of force constants.

APPENDIX

Terms occuring in Green's function elements:

$$Q_{x4} = (bK1 - aK3)/\sqrt{(a^2+b^2)}$$

$$Q_{x5} = (aK1 - \sqrt{(a^2+b^2)}\,K2 + bK3)/\sqrt{2(a^2+b^2)}$$

$$Q_{x6} = (aK1 + \sqrt{(a^2+b^2)}\,K2 + bK3)/\sqrt{2(a^2+b^2)}$$

$$Q_{z1} = (dK4 + CK6)/\sqrt{(c^2+d^2)}$$

$$Q_{z2} = (CK4 - \sqrt{(c^2+d^2)}\,K5 - dK6)/\sqrt{2(C^2+d^2)}$$

$$Q_{z3} = (CK4+\sqrt{(c^2+d^2)}\,K5-dK6)/\sqrt{2(c^2+d^2)}$$

$$K1 = -\sqrt{m_z/(m_z+m_z)}$$

$$K2 = \sqrt{3m_xm_y}\;C\beta/d_2(m_x+m_x)$$

$$K3 = -\sqrt{3m_xm_z}\;C\beta/\sqrt{M}\;d_3$$

$$d_2 = d_3/\sqrt{(m_x+m_z)}$$

$$d_3 = \sqrt{(m_x+m_z+3m_yC_\beta^2)}$$

$C\beta$ = cos (β); where β is the FNO angle

m_x, m_y and m_z are the resepctive atomic masses

$$M = (m_x+m_z+3m_y)$$

$$K4 = \sqrt{3m_y}\;S\beta/d_4$$

$$K5 = -3A\;S\beta\;\sqrt{m_y}/d_5\;\sqrt{m_x}$$

$$K6 = -0.6098 \text{ (for } ONF_3)$$

$$P = (m_zR-3m_yrC\beta)/M$$

$$I_x = 3m_y(rC\beta+p)^2+\tfrac{3}{2}\;m_yr^2S\beta^2+m_z(R-p)^2+m_xp^2$$

$$A = m_x\sqrt{m_y}\;S\beta/d_4^2$$

$$d_4 = \sqrt{(2m_x+3m_yS\beta^2)}$$

$$d_5^2 = 3[2A^2-2AS\beta\sqrt{m_y}+m_y+(3A^2S_\beta^2m_y/m_x)]$$

$S\beta$ = sin (β), and

R and r are the NO and NF bond lengths, respectively.

REFERENCES

[1] W. B. Fox, J. S. MacKenzie, N. Venderkooi, B. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, B. B. Stewart, *J. Am. Chem. Soc.* **88**, 2604 (1966).
[2] N. Bartlett, J. Passmore, E. J. Wells, *Chem. Comm.* 213 (1966).
[3] E. C. Curtis, D. Pilipovich, W. H. Moberly, *J. Chem. Phys.* **46**, 2904 (1967).
[4] W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, R. Juurik, *Inorg. Chem.* **7**, 2064 (1968).
[5] R. P. Hirschmann, D. F. Harnisch, J. R. Holmes, J. S. MacKenzie, W. B. Fox, *App. Spectrosc.* **23**, 333 (1969).
[6] S. Abramowitz, I. W. Levin, *J. Chem. Phys.* **51**, 463 (1969).
[7] C. V. Barney, A. D. Cormier, *J. Chem. Phys.* **58**, 4709 (1973).
[8] N. Aminadav, H. Selig, S. Abramowitz, *J. Chem. Phys.* **60**, 325 (1974).
[9] K. O. Christe, E. C. Curtis, C. J. Schack, *Spectrochim. Acta* **31**, 1035 (1975).

[10] V. Plato, W. D. Hartford, K. Hedberg, *J. Chem. Phys.* **53**, 3488 (1970).
[11] J. S. Ziomek, E. A. Piotrowski, *J. Chem. Phys.* **34**, 1087 (1961).
[12] J. H. Meal, S. R. Polo, *J. Chem. Phys.* **24**, 1119 (1956).
[13] S. Bhagavantham, T. Venkatarayadu, *Applications of Group Theory to Physical Problems*, Andhra University Press, Waltair 1962.
[14] R. E. Wames, T. Wolfram, *J. Chem. Phys.* **40**, 853 (1964).
[15] C. D. Bass, L. Lynds, T. Wolfram, R. E. DeWames, *J. Chem. Phys.* **40**, 3611 (1964).
[16] T. Wolfram, C. D. Bass, R. E. DeWames, L. Lynds, *Bull. Chem. Soc. Japan* **39**, 201 (1966).
[17] T. Wolfram, R. E. DeWames, *Bull. Chem. Soc. Japan* **39**, 207 (1966).
[18] S. J. Cyvin, *Spectrochim. Acta* **15**, 828 (1959).
[19] K. Ramaswamy, N. Mohan, *Z. Naturforsch.* **25b**, 169 (1960).
[20] K. Ramaswamy, G. Shanmugam, *Acta Phys. Pol.* **A41**, 3 (1972).