MOLECULAR CONSTANTS OF SOME NITROGEN HALOGEN COMPOUNDS BY GREEN'S FUNCTION ANALYSIS. II

By K. Ramaswamy and R. Namasivayam

Department of Physics, University of Annamalai, Annamalainagar*

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An attempt is made to apply Green's function and partitioning techniques to the case of bent *XYZ* type molecules. The isotopic rules have been formulated. The force constants, mean amplitudes of vibration, rotational distortion constants and Coriolis coupling constants have been computed and compared with other calculated and observed values, whichever is available. The agreement is quite good in all cases. The inertial defect for the ground vibrational state is also calculated.

1. Introduction

The determination of molecular constants from spectral data is greatly simplified when data for the isotopic modifications of the same molecule are available. This has been done successfully by the application of Green's function procedure to the problem of vibrational analysis by DeWames *et al.*, [1–4] and others [5–10] (reference [10] is part I of the series). However, the solution of the isotopic Green's function equations can become sizeable task for the more complicated case of an unsymmetrical molecule. But once the "mixing parameter matrix" is properly determined, it is wonderfully suited for the analysis of perturbed and substituted molecular systems.

In the present study, the isotopic rules for the "unsymmetrical *XYZ* bent type molecules" (ONF, ONCl and ONBr) were tried and obtained along with the other molecular constants. The isotopic product rules were verified.

2. Isotopic rules for $XYZ \rightarrow X^{(i)}YZ \rightarrow XY^{(i)}Z$

In Green's function approach to melocular dynamics the procedure is based upon the fact that the entire dynamics of a perturbed molecule is contained in Green's function for the unperturbed molecule. The bent *XYZ* type molecules studied belong to the C_s point group. All three vibrations are in-plane vibrations, all come under A' species.

* Address: Department of Physics, Annamalai University, Annamalainagar P.O., Tamilnadu, India.

The frequencies ω_1 and ω_2 are the $X-Y$ and $Y-Z$ stretching and ω_3 is the XYZ (α) bending.

In the case of a single isotopic substitution treating the isotopic molecule as a perturbed system, the secular determinant reduces to

$$|\varepsilon\omega^2 G(\omega^2)+I| = 0 \tag{1}$$

where $\varepsilon^{-1} = \dfrac{m^{(i)}-m}{m}$, in which m is the original mass and $m^{(i)}$ is the isotope mass. $G(\omega^2)$ is Green's function of the unperturbed molecule, ω is the vibrational frequency and I is the unit matrix. The determinant equation is automatically separated out according to the irreducible representations of the perturbed molecule. Green's function for the general motion of the molecule is given by

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

where ω_k's are the frequencies of vibration, rotation and translation (the frequencies corresponding to rotational and translational motions are zero) and l_{ik} is the ik^{th} element of the transformation matrix between the normal (Q) and the mass weighted cartesian coordinates (X) given by

$$X = lQ \tag{3}$$

The normal coordinates Q_i are linear combinations of the external symmetry coordinates S^E, through a mixing parameter. The normal coordinates for the bent XYZ type molecules can be written as

$$\begin{aligned} Q_1 &= S_1^E \\ Q_2 &= (S_2^E + pS_3^E)(1+p^2)^{-\frac{1}{2}} \\ Q_3 &= (S_3^E - pS_2^E)(1+p^2)^{-\frac{1}{2}} \end{aligned} \tag{4}$$

where S_1^E is a pure $X-Y$ stretch; the S_2^E $Y-Z$ stretch and the S_3^E $XYZ(\alpha)$ bending are considerably mixed in all the molecules studied. p is the mixing parameter. The isotopic rules for both the substitutions $X \rightarrow Y^{(i)}$ and $Y \rightarrow Y^{(i)}$ were obtained for all the molecules and are given in the Appendix. As the isotopic rules obtained are quite complicated, they are given in abbreviated forms with suitable contractions. The product rule (Eq. (17)) is verified in all the cases, what is shown in Table I.

3. Molecular constants

(a) Potential energy constants: The potential energy constants were evaluated in the usual way [10] from a knowledge of the mixing parameter. To determine the mixing parameter, Green's function matrix and the vibrational frequencies of perturbed and unperturbed molecules were used. The vibrational wavenumber [11–13] of perturbed and unperturbed molecules, the internuclear distances and interbond angles [11, 14, 15]

TABLE I

Vibrational wavenumbers, molecular parameters (including references) and isotopic rules for some *XYZ* bent type molecules

Molecules	Vibrational wave numbers (cm^{-1})				Molecular parameters					Isotopic product rule $\frac{\omega_1^{(i)2}\omega_2^{(i)2}\omega_3^{(i)2}}{\omega_1^2\omega_2^2\omega_3^2}$	
	ω_1	ω_2	ω_3	Ref.	r_{X-Y}	d_{Y-Z}	q_{X-Z}	α (XYZ)	Ref.	Observed	Calculated
$O^{16}N^{14}F$	1876.8	522.9	775.5							0.9131	0.9134*
$O^{16}N^{15}F$	1843.9	520.4	757.9	[11]	1.13Å	1.52Å	2.18Å	110°	[11]	0.8966	0.8961
$O^{18}N^{14}F$	1827.1	514.1	767.2								
$O^{16}N^{14}Cl$	1835.6	336.4	603.2							0.9085	0.9060
$O^{16}N^{15}Cl$	1803.6	334.3	588.8	[12]	1.139Å	1.975Å	2.642Å	113° 20′	[14]	0.8842	0.8835
$O^{18}N^{14}Cl$	1786.1[a]	329.3	595.5								
$O^{16}N^{14}Br$	1832.3	269.2	548.0							0.9002	0.9011
$O^{16}N^{15}Br$	1800.4	267.0	533.5	[13]	1.15Å	2.14Å	2.81Å	114°	[15]	0.8722	0.8716
$O^{18}N^{14}Br$	1783.0	261.7[a]	541.0[a]								

a — Values from force constants.
* This number of significant digits is retained to secure internal consistency in the calculation.

are listed in Table I. Green's function $G(\omega^2)$ for the end atom substitution $(X \rightarrow X^{(i)})$ and the central atom substitution $(Y \rightarrow Y^{(i)})$ are given by expressions (5) and (6), respectively:

$$\begin{vmatrix} \varepsilon\omega^2 G_{11}(\omega^2)+1 & \varepsilon\omega^2 G_{12}(\omega^2) \\ \varepsilon\omega^2 G_{21}(\omega^2) & \varepsilon\omega^2 G_{22}(\omega^2)+1 \end{vmatrix} = 0 \qquad (5)$$

$$\begin{vmatrix} \varepsilon\omega^2 G_{33}(\omega^2)+1 & \varepsilon\omega^2 G_{34}(\omega^2) \\ \varepsilon\omega^2 G_{43}(\omega^2) & \varepsilon\omega^2 G_{44}(\omega^2)+1 \end{vmatrix} = 0 \qquad (6)$$

where $\varepsilon = [m_x^{(i)} - m_x]/m_x$ in (5) and $\varepsilon = [m_y^{(i)} - m_y]/m_y$ in (6), in which $m_x^{(i)}$ and $m_y^{(i)}$ are the masses of the isotopes of m_x and m_y, the mass of the end and the central atoms of the molecules, respectively. G_{11}, G_{12} $(= G_{21})$, G_{22}, G_{34} $(= G_{43})$ and G_{44} are the elements of Green's function matrix and ω's are the vibrational frequencies in cm^{-1}. From the isotopic sum rule (Eg. (15)) the mixing parameter is determined. The force constants calculated are listed in Table II.

(b) Mean amplitudes of vibration: The mean amplitude quantities for all the cases were obtained from the mean square amplitude quantities evaluated by the method of Cyvin [16] as outlined earlier [10]. This value for nonbonded distance is determined by the method of Ramaswamy *et al.* [17]. The results are given in Table III.

TABLE II

Force constants of bent XYZ type molecules (in mdynes/Å)

	ONF			ONCl			ONBr		
	$X\rightarrow X^{(i)}$[b]	$Y\rightarrow Y^{(i)}$	Ref.	$X\rightarrow X^{(i)}$	Ref.	$Y\rightarrow Y^{(i)}$	$X\rightarrow X^{(i)}$	Ref.	$Y\rightarrow Y^{(i)}$
f_r	15.7491	15.7068[a]PC*		15.1833 PC		15.3086 PC	15.3991 PC		15.3987 PC
		15.833	[26]	15.26	[12]		15.250	[13]	
		15.900	[11]	14.92	[28]		14.300	[27]	
		15.300	[27]	14.133	[26]		14.210	[28]	
		15.079	[25]	14.12	[27]		14.157	[26]	
f_d	2.0390	3.0111 PC		2.3862 PC		2.6926 PC	1.3366 PC		1.3751 PC
		3.320	[28]	2.246	[26]		1.300	[27]	
		2.791	[26]	2.190	[28]		1.130	[13]	
		2.300	[11]	1.720	[31]		2.16	[28]	
		2.090	[25]	1.270	[12]		2.21	[26]	
f_{rd}	0.9550	1.1515 PC		1.1374 PC		1.2409 PC	1.1011 PC		1.1076 PC
		1.850	[25]	1.000	[27]		1.200	[27]	
		2.500	[11]	1.53	[12]		1.470	[13]	
		0.121	[26]						
f_α	1.0489	0.7318 PC		0.3040		0.2949 PC	0.3634 PC		0.3559 PC
		0.7510	[26]	0.300	[26]		0.2602	[28]	
		0.6288	[25]	0.3067	[28]		0.4592	[13]	
		1.0480	[11]	0.5868	[12]		0.4551	[27]	
		0.4075	[28]	0.5600	[27]		0.2040	[26]	
$f_{r\alpha}$	0.2589	0.1188 PC		0.2333 PC		0.2510 PC	0.3772 PC		0.3729 PC
		0.1430	[26]	0.0667	[12]		0.0701	[13]	
		0.2068	[11]	0.064	[26]		0.0520	[26]	
$f_{d\alpha}$	0.1911	0.3164 PC		0.2229 PC		0.3453PC	0.0248 PC		0.0220 PC
		0.1894	[25]	0.1310	[26]		0.0638	[20]	
		0.2780	[26]	0.080	[12]		0.115	[26]	
		0.1526	[11]						

PC* — refers to the present calculation.

a — This number of significant digits is retained to secure internal consistency in the calculation.

b — Ref. [10].

(c) Rotational distortion constants: The rotational distortion parameters $\tau\alpha\beta\gamma\delta$ can be obtained from the theoretical formulation for vibration-rotation interaction by Wilson and Howard [18] and Nielsen [19]. The parameters are defined [20] as

$$\hbar^4\tau\alpha\beta\gamma\delta = -\frac{K}{I^0_{\alpha\alpha}I^0_{\beta\beta}I^0_{\gamma\gamma}I^0_{\delta\delta}}\sum_i \frac{a_i^{(\alpha\beta)}a_i^{(\gamma\delta)}}{\omega_i^2} \tag{7}$$

TABLE III

Mean amplitudes of vibration for bent XYZ type molecules (bonded and non-bonded) in Å at 298.16°K (XYZ) (α) is in radians)

	ONF			ONCl			ONBr		
	$X\rightarrow X^{(i)}$[b]	$Y\rightarrow Y^{(i)}$	Ref.	$X\rightarrow X^{(i)}$	Ref.	$Y\rightarrow Y^{(i)}$	$X\rightarrow X^{(i)}$	Ref.	$Y\rightarrow Y^{(i)}$
$X-Y$	0.034767	0.034769[a] PC*		0.035121 PC		0.035115 PC	0.035291 PC		0.035291 PC
		0.0355	[11]	0.0362	[12]		0.0356	[13]	
$Y-Z$	0.059528	0.053414 PC		0.055490		0.054946 PC	0.065511 PC		0.064775 PC
		0.0571	[11]	0.0703	[12]		0.0722	[13]	
XYZ (α)	0.050432	0.056907 PC		0.061370 PC		0.064389 PC	0.051087 PC		0.051648 PC
		0.0633	[11]	0.0702	[12]		0.0732	[13]	
$X...Z$	0.061829	0.064282 PC		0.087028 PC		0.070562 PC	0.079687 PC		0.079892 PC
		0.0605	[11]	0.0730	[12]		0.0775	[13]	

PC* — refers to the present calculation.

a — This number of significant digits is retained to secure internal consistency in the calculation.

b — Ref. [10].

where α, β, γ, and δ can be in turn x, y or z. If these parameters are expressed in MHz/sec., the constant K assumes the value 5.7498×10^8. The vibrational frequencies are in cm^{-1} and the principal components of the tensor of moments of inertia $I^0_{\alpha\alpha}$, evaluated for the

TABLE IV

Rotational distortion constants (in MHz/sec) and Coriolis coupling constants for some XYZ bent type molecules

	ONF			ONCl			ONBr		
	$X\rightarrow X^{(i)}$*	$Y\rightarrow Y^{(i)}$	Ref.	$X\rightarrow X^{(i)}$	Ref.	$Y\rightarrow Y^{(i)}$	$X\rightarrow X^{(i)}$	Ref.	$Y\rightarrow Y^{(i)}$
D_J	3.144[a]	2.437		3.003		2.694	0.901		0.961
D_K	3.143	2.496		3.049		2.710	0.919		0.984
D_{JK}	−6.281	−4.923		−6.050		−5.403	−1.817		−1.940
R_5	1.046	0.833		1.017		0.906	0.304		0.326
R_6	−0.521	−0.418		−0.510		−0.460	−0.149		−0.160
δ_J	2.087	1.626		2.010		1.805	0.598		0.639
ζ_{12}	−0.111	−0.545 PC		−0.460 PC		−0.567 PC	−0.308 PC		−0.325 PC
		−0.128	[11]	−0.135	[12]		−0.143	[13]	
ζ_{13}	0.879	0.698 PC		0.845 PC		0.776 PC	0.905 PC		0.898 PC
		0.834	[11]	0.918	[12]		0.940	[13]	
ζ_{23}	−0.465	−0.465 PC		−0.348 PC		−0.348 PC	−0.297 PC		−0.297 PC
		−0.536	[11]				−0.310	[13]	

* — Ref. [10].

a — as in Table I.

ground state in the centre of mass of the molecule, and the coefficients $a_i^{(\alpha\beta)}$ are expressed in amu A^{02}. The coefficients $a_i^{(\alpha\beta)}$ are related to "l" matrix elements [21] as follows:

$$a_i^{(\alpha\alpha)} = 2\sum_k m_k^{\frac{1}{2}}[\beta_k^0 l_{ki}^{(\beta)} + \gamma_k^0 l_{ki}^{(\gamma)}] \tag{8}$$

$$a_i^{(\alpha\beta)} = -2\sum_k m_k^{\frac{1}{2}}\alpha_k^0 l_{ki}^{(\beta)} \ldots (\alpha \neq \beta) \tag{9}$$

where α_k^0, β_k^0 and γ_k^0 represent the equilibrium cartesian coordinates and m_k, the mass of the k^{th} atom.

In the present investigation, the orientation of the molecule-fixed axes was taken so that the molecule lies in the xy plane and the z-axis is perpendicular to the plane. For a planar molecule,

$$I_{zz}^0 = I_{xx}^0 + I_{yy}^0 \tag{10}$$

So, from group theoretical considerations among the nine nonvanishing τ's for a planar molecule the two parameters (τ_{xzxz} and τ_{yzyz}) are zero (because coordinates related to the

TABLE V

Inertial defect Δ in amu A^{02} and verification of the relations $a_i^{(xx)} + a_i^{(yy)} = a_i^{(zz)}$[23] for some XYZ bent type (planar)molecules

$X \rightarrow X^{(i)}$	Ref.	$Y \rightarrow Y^{(i)}$	Ref.	$X \rightarrow X^{(i)}$	Ref.	$Y \rightarrow Y^{(i)}$	Ref.	$X \rightarrow X^{(i)}$	Ref.	$Y \rightarrow Y^{(i)}$	Ref.
0.1124[a]PC 0.1165Obs 0.1170	[25] [11]	0.1236PC 0.1165	[25]	0.1589PC 0.148	[12]	0.168 PC 0.148	[12]	0.1574 PC 0.147	[12]	0.1587 PC 0.147	[13]

	$X \rightarrow X^{(i)}$		$Y \rightarrow Y^{(i)}$	
	$a_i^{(xx)} + a_i^{(yy)}$	$a_i^{(zz)}$	$a_i^{(xx)} + a_i^{(yy)}$	$a_i^{(zz)}$
		ONF		
Q_1	6.459716[a]	6.459714	6.459712	6.459714
Q_2	1.541786	1.541786	−7.559050	−7.559054
Q_3	11.960970	11.960970	−9.673504	−9.673500
		ONCl		
Q_1	6.861144	6.861146	6.861146	6.861146
Q_2	−7.610576	−7.610576	−9.650822	−9.650822
Q_3	−15.949266	−15.964702	−14.820620	−14.820620
		ONBr		
Q_1	7.051620	7.051632	7.051632	7.051632
Q_2	21.479364	21.479369	21.228120	21.228210
Q_3	7.309184	7.309184	7.720612	7.720612

a — as in Table I.

axis perpendicular to the molecular plane are all zero at equilibrium). The rest of the seven τ-parameters are computed and from them the rotational distortion constants D_J, D_K, D_{JK}, R_5, R_6 and δ_J are obtained using the expressions of Kivelson and Wilson [22], appropriately modifying to suit symmetry and orientation of the molecules in the present study. The values are given in Table IV.

The relation (Eq. (22) of Ref. [23])

$$a_i^{(xx)} + a_i^{(yy)} = a_i^{(zz)} \tag{11}$$

where i refers to the i^{th} normal coordinate of the in-plane vibration because a planar molecule is found to exist perfectly for all three vibrational modes of the molecules studied for both the substitutions, the result of which is shown in Table V.

(d) Coriolis coupling constants and inertial defect: Coriolis coupling constants were obtained using Meal and Polo's equation [24],

$$\zeta^{(i)} = lM^{(i)}l^* \tag{12}$$

where $i = (x, y, z)$ denotes the axis of rotation and $M^{(i)}$ is a block diagonal supermatrix made up of indentical (3×3) submatrices, one for each atom. l^* is a transpose of l (Eq. (12)). The values evaluated are given in Table IV.

The inertial defect Δ for a planar molecule in the ground vibrational state is calculated from the relation [25]

$$\Delta = \left(\frac{h}{2\pi^2 c}\right)[\omega_1^{-1} + \omega_2^{-1} - (\omega_1 + \omega_2)^{-1}]\zeta_{12}^2 + [\omega_2^{-1} + \omega_3^{-1} - (\omega_2 + \omega_3)^{-1}]\zeta_{23}^2$$

$$+ [\omega_3^{-1} + \omega_1^{-1} + (\omega_3 + \omega_1)^{-1}]\zeta_{13}^2 \tag{13}$$

where $h/2\pi^2 c = 67.4505$; ω_1, ω_2 and ω_3 are vibrational frequencies; ζ_{12}, ζ_{13} and ζ_{23} are the Coriolis coupling constants. The inertial defect values are listed in Table V.

4. Discussion

As already seen [10], Green's function and partitioning techniques can be applied to the *XYZ* bent type molecules of very low symmetry, also bypassing the force constant model, to calculate the molecular constants which are exact, self-consistent and compare well with other values. The isotopic rules are predicted and the product rule (Eq. (17)) agrees well with the well known Teller-Redlich product rule [34] for isotopic substitution. The equation (15) is a sum rule for the frequencies which is used to determine the mixing parameter, used in the finding of values for molecular constants which are in good agreement with reported values. From Table II it is seen that the values of the symmetrized force constants, obtained hereby applying Green's function analysis, are in general in good agreement with the earlier results obtained by different techniques. The calculated f_r (NO stretching) values in all three molecules for both substitutions agree very well with those obtained by Jones *et al.* [11, 12, 13] and Sawodny *et al.* [26], even though the present

values are slightly different from those reported by Cook [25], Mirri and Mazzariol [27] and Devlin and Hisatsune [28]; however, this value in ONCl for $O^{16} \rightarrow O^{18}$ substitution (15.18 mdynes/Å) agrees well with the value of 15.00 mdynes/Å of Devlin and Hisatsune [28]. This value is practically the same for all three molecules for both substitutions. In ONF, this value (15.8 mdynes/Å) is very near the value (15.9 mdynes/Å) [11] in free NO, showing that the F atom does not greatly affect the NO bond which is contributed by the structure given below: Cook [25] obtained this value (15.08 mdynes/Å) in the range $13.0 \leqslant f_r \leqslant 15.9$ mdynes/Å. This value for ONCl (15.18 and 15.31 mdynes/Å) is significantly lower, what indicates greater interaction of chlorine with NO than of fluorine with NO in these nitrosyl halides. This value in ONBr (15.4 mdynes/Å) is also lower than in ONF, which finds the same explanation as above. The f_d(N-halide) force constant

Fig. 1

of 3.0 mdynes/Å in ONF, 2.39 and 2.69 mdynes/Å in ONCl and 1.34 and 1.38 mdynes/Å in ONBr agree well with those by Devlin and Hisatsune [28] and Sawodny *et al.* [26] (ONF and ONCl), and Mazzariol [27] (ONBr). In NF_3 this value is 4.4. mdynes/Å [29], what, is in agreement with the longer distance of NF.

Regarding the nature of bonding Sprately and Pimentel [30] found from the force constants that the main bond joining the halide to the NO group consists of an overlap of a singly occupied valence orbital of the halide with a singly occupied π^* orbital of NO. The resulting increase (or decrease) in electron density in this NO π^* orbital would cause a decrease (or increase) in the NO bond strength compared with that of free NO. For ONF, the NO stretching constant is the same as that for free NO, indicating little change in electron density in the NO π^* orbital. For ONCl and ONBr, the force constant is significantly lower, showing that the heavier halides, which are better electron donors, contribute more electron density to the NO π^* orbital. The N-halide bond strength decreases from F to Cl to Br, as expected, because of the increased mass and bond strength. Among these three molecules nothing can be concluded about the differences in N halide bonding due to the lack of data for bond order calculation. The α-bending constant follows the same trend as the N-halide stretching constant. This value in ONF (0.73 mdynes/Å for central atom substitution) is nearer to the values of Sawodny *et al.* [26] (0.75 mdynes/Å) and Cook [25] (0.63 mdynes/A); in ONCl 0.3 mdynes/Å agrees well with the values by Sawodny *et al.* [26] (0.3 mdynes/Å) and Devlin and Hisatsune [28] (0.31 mdynes/Å) and in ONBr, 0.36 mdynes/Å, nearer to the value by Sawodny *et al.*, [26] and Devlin and Hisatsune [28]. In all these molecules, there is repulsi onbetween the oxygen and the halogen atoms This repulsion and distortion leads to a longer and weaker N-halide bond, thereby increasing the angle α. Due to this in ONF and ONCl, the nitrogen halide distances are more than 10 per cent longer than a single normal bond [14]. The N-halide bond must involve

a partly occupied antibonding π orbital of NO and a p orbital of the halide, but it seems that the oxygen-halide interaction must be considered also in describing the electronic structure. The interaction constants, in general, agree with the reported values. The NO, NX (X = F, Cl, Br) interaction is quite large and this interaction constant (f_{rd}) in all the molecules (both the substitutions) is 1.1 mdynes/Å, which agrees with the value of about 1.0 mdynes/Å reported by Mirri and Mazzariol [27]. So the bonding is quite similar for these molecules. The other interactions are fairly low. The large NO, NX interaction indicates considerable electronic rearrangement if one bond is constrained in a displaced position.

The mean amplitudes of vibration (Table III) and Coriolis coupling constants (Table IV) are in good agreement with the values calculated by Jones *et al.* [11–13]. No experimental values are available for comparison. The $\tau_{\alpha\beta\gamma\delta}$ parameter and the rotational distortion constants agree well with Cook's value [25] for ONF. The verification of the relation (11) [23] among the coefficients $a_i^{(\alpha\beta)}$ of the normal coordinates Q_i in the power series of $I^0_{\alpha\beta}$, the moment of inertia (Table IV) for all the three modes of vibration, studies the "planarity of the molecules". This helps to investigate the "inertial defect" of a planar molecule. The "inertial defect" value (0.1124 and 0.1236 amu Å^2) (Table V) agree well with calculated (0.1162 amu Å^2) [25] and observed (0.1165 amu Å^2) values [25] of Cook for ONF. This agreement in other molecules is also fair. This is observed from the relation $\Delta = I_C - I_A - I_B$ [11] for a planar molecule (I_C is the largest moment of inertia). At equilibrium Δ should be zero for a planar molecule. However, this Δ is expressed [21, 25] as a function of the vibrational frequencies and the Coriolis coupling constants (Eq. (13)). This factor is sensitive to force constants. There is a small discrepancy between the calculated value of Δ and the observed value, which is believed to be due to an electronic contribution not considered in the calculation. This contribution arises from the out-of-plane π electrons of the N = O bond and is opposite in sign to the vibrational contribution it thus tends to lower the observed value (Table V). The Coriolis coupling constants obtained obey the sum rule [32, 33].

$$(\zeta_{12}^{(z)})^2 + (\zeta_{13}^{(z)})^2 + (\zeta_{23}^{(z)})^2 = 1 \tag{14}$$

The molecular constants were determined for the molecules ONF, ONCl and ONBr for both substitutions ($X \rightarrow X^{(i)}$ and $Y \rightarrow Y^{(i)}$); no pronounced change is observed in the constant values. In the force constant values there is a difference in the N-halide force constant (f_d) in ONF and ONCl. Rotational distortion constants show some difference in ONF between the two substitutions. Slight changes are observed in Coriolis coupling constants. Due to this substitution no change is observed when checking the relation $a_i^{(xx)} + a_i^{(yy)} = a_i^{(zz)}$ which is exactly the same in both the substitutions.

APPENDIX

Isotopic rules for the substitution $XXY \rightarrow X^{(i)}YZ \rightarrow XY^{(i)}Z$:

$$\omega_1^{(i)^2} + \omega_2^{(i)^2} + \omega_3^{(i)^2} =$$

$$= \frac{K(\omega_1^2+\omega_2^2+\omega_3^2) + L(\omega_1^2+\omega_2^2) + M(\omega_2^2+\omega_3^2) + Q(\omega_3^2+\omega_1^2) + R\omega_1^2 + T\omega_2^2 + U\omega_3^2}{K+L+M+Q+R+T+U} \tag{15}$$

$$\omega_1^{(i)^2}\omega_2^{(i)^2}+\omega_2^{(i)^2}\omega_3^{(i)^2}+\omega_3^{(i)^2}\omega_1^{(i)^2} =$$

$$=\frac{K(\omega_1^2\omega_2^2+\omega_2^2\omega_3^2+\omega_3^2\omega_1^2)+L\omega_1^2\omega_2^2+M\omega_2^2\omega_3^2+Q\omega_3^2\omega_1^2}{K+L+M+Q+R+T+U} \cdots \quad (16)$$

$$\omega_1^{(i)^2}\omega_2^{(i)^2}\omega_3^{(i)^2} = \frac{K}{K+L+M+Q+R+T+U}\omega_1^2\omega_2^2\omega_3^2 \quad (17)$$

where K, L, M, Q, R, T and U are contractions which are too complicated expressions to give here. These contractions, involving p, the mixing parameters ε which is equal to $m_x^{(i)}-m_x/m_x$ for the substitution in the X (end) atom and $m_y^{(i)}-m_y/m_y$ for the substitution in Y (central) atom of the molecule, and other factors involving mass of the atoms, molecular parameters *etc.*, are not given here. But the contractions K, L, M *etc.*, are given in quadratic equations in p, the mixing parameter with numerical coefficients.

Nitrozyl fluoride (ONF) molecule-O-Substitution:

$$\begin{aligned}
K &= (54.604399\,p^2+54.604399)\,p^2\\
L &= 0.053149\,p^2+0.153264\,p+3.000179)P^2\\
M &= (1.275335\,p^2+1.275335)\,P^2\\
Q &= (3.000162\,p^2+0.142044\,p+0.053149)\,P^2\\
R &= (0.002820\,p^2+0.002820)\,P^2\\
T &= (0.001089\,p^2-0.027147\,p+2.578462)\,P^2\\
U &= (0.065218\,p^2+0.027147\,p+2.514334)\,P^2
\end{aligned}$$

Nitrosyl fluoride (ONF) molecule-N-substitution:

$$\begin{aligned}
K &= (50.316995\,p^2+50.316995)\,P^2\\
L &= (2.099129\,p^2-1.632006\,p+0.693683)\,P^2\\
M &= (1.870955\,p^2+1.870955)\,P^2\\
Q &= (0.693274\,p^2+1.622087\,p+2.088735)\,P^2\\
R &= (0.015706\,p^2+0.015706)\,P^2\\
T &= (0.077097\,p^2-0.067212\,p+0.014649)\,P^2\\
U &= (0.014649\,p^2+0.067212\,p+0.077079)\,P^2
\end{aligned}$$

Nitrosyl chloride (ONCl) Molecule-O-substitution:

$$\begin{aligned}
K &= (105.255793\,p^2+105.255793)\,P^2\\
L &= (0.293140\,p^2+1.275944\,p+7.071294)\,P^2\\
M &= (5.983998\,p^2+5.983998)\,P^2\\
Q &= (7.071232\,p^2-1.275944\,p+0.293140)\,P^2\\
R &= (0.016249\,p^2+0.016249)\,P^2\\
T &= (-0.004262\,p^2-0.047560\,p+5.412588)\,P^2\\
U &= (0.176987\,p^2+0.047560\,p+5.231333)\,P^2
\end{aligned}$$

Nitrosyl chloride molecule (ONCl)-N-substitution:

$$K = (97.905951\,p^2+97.905951)\,P^2$$
$$L = (4.600660\,p^2-2.714859\,p+1.776533)\,P^2$$
$$M = (3.555979\,p^2+3.555979)\,P^2$$
$$Q = (1.776527\,p^2+2.305179\,p+4.600666)\,P^2$$
$$R = (0.043784\,p^2+0.043784)\,P^2$$
$$T = (0.160639\,p^2-0.166629\,p+0.043211)\,P^2$$
$$U = (0.043211\,p^2+0.166630\,p+0.160639)\,P^2$$

Nitrosyl Bromide (ONBr) Molecule-O-substitution:

$$K = (155.863072\,p^2+155.863072)\,P^2$$
$$L = (1.107924\,p^2+5.508762\,p+12.188051)\,P^2$$
$$M = (9.037248\,p^2+9.037248)\,P^2$$
$$Q = (12.187997\,p^2-5.508763\,p+1.107916)\,P^2$$
$$R = (0.037961\,p^2+0.037961)\,P^2$$
$$T = (0.009942\,p^2+0.151446\,p+0.576773)\,P^2$$
$$U = (0.576773\,p^2-0.151446\,p+0.009942)\,P^2$$

Nitrozyl Bromide (ONBr) Molecule-N-substitution:

$$K = (146.042449\,p^2+146.042449)\,P^2$$
$$L = (7.724017)\,p^2-5.352324\,p+2.650324)\,P^2$$
$$M = (5.245519\,p^2+5.245519)\,P^2$$
$$Q = (2.650378\,p^2+5.352444\,p+7.724025)\,P^2$$
$$R = (0.091133\,p^2+0.091133)\,P^2$$
$$T = (0.258486\,p^2-0.245224\,p+0.058161)\,P^2$$
$$U = (0.058161\,p^2+0.245224\,p+0.258486)\,P^2$$

where $P^2 = 1+p^2$.

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