

MOLECULAR CONSTANTS OF SOME NITROGEN-OXYGEN COMPOUNDS; GREEN'S FUNCTION ANALYSIS

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(Received April 17, 1971)

Green's function analysis of substituted and perturbed molecules proposed by DeWames and Wolfram was applied to the vibrational study of some nitrogen-oxygen compounds. The potential energy constants, mean amplitudes of vibration, Coriolis coupling constants and the rotational distortion constants were evaluated and found to be in very good agreement with the experimental values.

1. Introduction

The chemical bonding of nitrogen with oxygen is of considerable interest because of the presence of a variety of valence states that are available in these compounds. In addition, the isotopic compounds of nitrogen are easily available. Thus, these compounds come in handy in studying the isotopic rules and in the evaluation of unambiguous force fields. It has been shown [1-3] recently, that Green's function analysis presents itself as an elegant method in developing the isotopic rules and in evaluating all the molecular constants. The present paper deals with the derivation of the isotopic rules, calculation of molecular constants of various isotopes of NO_2^- and NO_3^- groups.

2. Frequency calculation of isotopic molecules

Using the observed vibrational frequencies of the unperturbed molecule $^{14}\text{N}^{16}\text{O}_2^-$ and those of the perturbed molecules $^{15}\text{N}^{16}\text{O}_2^-$, the mixing parameter was calculated as outlined by DeWames and Wolfram [1]. In the case of the symmetric substitution, $\text{YXY} \rightarrow \text{YX}^i\text{Y}$ or Y^iXY^i , the isotopic rules were given by DeWames and Wolfram as

$$\omega_1^i \omega_2^i = \omega_1^0 \omega_2^0 \left(\frac{m_y}{m_i} \right)^2 \left(\frac{m_x}{m_i} \right) \left[\frac{2m_y + m_x^i}{2m_y + m_x} \right] \quad (1)$$

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$$\omega_1^{i^*} + \omega_2^{i^*} = \frac{A^2(\omega_1^2 + \omega_2^2)(2m_y + m_x) + [(m_x^i/m_x)(m_y/m_y) - 1][2m_y a^2 \omega_2^2 + 2m_y \omega_1^2 + m_x(A^2(\omega_1^2 + \omega_2^2))]}{A^2(2m_y + m_x)(m_x^i/m_x)} \quad (2)$$

$$\omega_3^{i^*} = \omega_3^2 \left(\frac{m_y}{m_y^i} \right) \left(\frac{m_x}{m_x^i} \right) \left[\frac{m_x^i + 2m_y^i \sin^2 \alpha}{m_x + 2m_y \sin^2 \alpha} \right] \quad (3)$$

where $A^2 = (1+a^2)$ and a is the mixing parameter; ω_1 , ω_2 and ω_3 are the fundamental vibrational frequencies of the parent molecule and with the superscript i are those of the perturbed molecule, α is the interbond angle and m_x , m_y , m_x^i and m_y^i are the masses of the respective atoms.

TABLE I

Zero-order experimental frequencies [9, 10] used in the calculation of the mixing parameter, a

Molecule	Frequencies in cm^{-1}			a	Interbond angle α
	ω_1	ω_2	ω_3		
$^{14}\text{N}^{16}\text{O}_2$	1357.8	756.8	1665.5	1.00153	$134^\circ 15'$
$^{15}\text{N}^{16}\text{O}_2$	1342.5	747.1	1628.0	—	
$^{14}\text{N}^{16}\text{O}_2^-$	1316.2	798.1	1275.0	1.57549	115°
$^{15}\text{N}^{16}\text{O}_2^-$	1294.2	793.0	1249.5	1.49682	
$^{14}\text{N}^{16}\text{O}_3^-$	1054.8	1383.2	715.6	0.832962	120°
$^{15}\text{N}^{16}\text{O}_3^-$	1055.1	1352.3	714.4	0.802484	

For the unsymmetric substitution, $\text{YXY} \rightarrow \text{Y}^i\text{XY}$, the equations were given as

$$\omega_1^{i^*} + \omega_2^{i^*} + \omega_3^{i^*} = A_{11}\omega_1^2 + A_{22}\omega_2^2 + A_{33}\omega_3^2 \quad (4)$$

$$\omega_1^{i^*}\omega_2^{i^*} + \omega_2^{i^*}\omega_3^{i^*} + \omega_3^{i^*}\omega_1^{i^*} = A_{12}\omega_1^2\omega_2^2 + A_{23}\omega_2^2\omega_3^2 + A_{31}\omega_3^2\omega_1^2 \quad (5)$$

$$\omega_1^{i^*}\omega_2^{i^*}\omega_3^{i^*} = A_{123}\omega_1^2\omega_2^2\omega_3^2 \quad (6)$$

where the A 's have the same meaning as in reference [1]. Using these relations, the frequencies were calculated and are given in Table II.

Green's function for the planar XY_3 molecules has been derived by Bass *et al.* [2]. For the substitution $\text{XY}_3 \rightarrow \text{X}^i\text{Y}_3$ the isotopic rules given are

$$\omega_2^{i^*}\omega_3^{i^*} = A_{23}\omega_2^2\omega_3^2 \quad (7)$$

$$\omega_2^{i^*} + \omega_3^{i^*} = A_{22}\omega_2^2 + A_{33}\omega_3^2 \quad (8)$$

where the A 's have the same meaning as in reference [2]. The symmetric stretch frequency ω_1 does not shift and the out-of-plane frequency ω_4 becomes

$$\omega_4^{i^*} = \omega_4^2 \left(\frac{m_x}{m_x^i} \right) \left(\frac{m_x^i + 3m_y}{m_x + 3m_y} \right) \quad (9)$$

TABLE II

Observed and calculated frequencies (cm^{-1}) for the various isotopes of NO_2^- and NO_3^- molecules

Molecule	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
$^{14}\text{N}^{18}\text{O}_2^-$	(Calc.) ^a 1279.23	760.9	1247.6			
	(Obs.) ^b 1282.1	759.9	1248.8			
$^{15}\text{N}^{18}\text{O}_2^-$	(Calc.) 1256.1	756.6	1221.4			
	(Obs.) —	—	1221.5			
$^{14}\text{N}^{16}\text{O}^{18}\text{O}^-$	(Calc.) 1307.3	782.3	1258.2			
	(Obs.) 1303.9	779.0	1256.6			
$^{15}\text{N}^{16}\text{O}^{18}\text{O}^-$	(Calc.) 1279.6	777.6	1231.7			
	(Obs.) —	—	1230.4			
$^{14}\text{N}^{18}\text{O}_3^-$	(Calc.) 994.6	1351.9	690.4	830.7		
	(Obs.) 994.4	1363.4	—	830.6		
$^{15}\text{N}^{18}\text{O}_3^-$	(Calc.) 993.81	1321.4	682.7	809.5		
	(Obs.) —	1329.3	—	—		
$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$	(Calc.) 1041.9	1362.3	708.0	1372.4	699.6	836.3
	(Obs.) 1034.9	1371.1	—	1383.2	—	837.8
$^{15}\text{N}^{16}\text{O}_2^{18}\text{O}^-$	(Calc.) 1034.4	1334.5	707.1	1339.6	713.5	816.4
	(Obs.) —	1338.7	—	1352.3	—	816.4
$^{14}\text{N}^{16}\text{O}^{18}\text{O}_2^-$	(Calc.) 1011.7	1371.5	700.3	1348.6	692.3	832.8
	(Obs.) 1014.3	1377.2	—	1363.4	—	843.3
$^{15}\text{N}^{16}\text{O}^{18}\text{O}_2^-$	(Calc.) 1019.4	1349.3	693.8	1323.7	678.5	809.3
	(Obs.) —	1344.7	—	1329.3	—	—

a — Present work; b — Reference [10]

For the other symmetric substitution $\text{XY}_3 \rightarrow \text{XY}_3^i$, the isotopic rules were given as

$$\omega_1^{i^2} = \omega_1^2 \left(\frac{m_y}{m_y^i} \right) \quad (10)$$

$$\omega_2^{i^2} \omega_3^{i^2} = A'_{23} \omega_2^2 \omega_3^2 \quad (11)$$

$$\omega_2^{i^2} + \omega_3^{i^2} = A'_{22} \omega_2^2 + A'_{33} \omega_3^2. \quad (12)$$

The out-of-plane frequency is calculated from Eq. (9).

For the unsymmetric substitution $\text{XY}_3 \rightarrow \text{XY}_2\text{Y}^i$ or XYY_2^i , the normal vibrations change as given below:

$$\text{XY}_3(D_{3h}) \rightarrow \text{XY}_2\text{Y}^i(C_{2v})$$

$$\omega_1(A') \rightarrow \omega_1(A_1)$$

$$\omega_2(E') \rightarrow \omega_2(A_1) + \omega_4(B_2)$$

$$\omega_3(E') \rightarrow \omega_3(A_1) + \omega_5(B_2)$$

$$\omega_4(A'') \rightarrow \omega_6(B_1).$$

The isotopic rules are

$$\omega_1^{i^2}\omega_2^{i^2}\omega_3^{i^2} = B_{123}\omega_1^2\omega_2^2\omega_3^2 \quad (13)$$

$$\omega_1^{i^2} + \omega_2^{i^2} + \omega_3^{i^2} = B_{11}\omega_1^2 + B_{22}\omega_2^2 + B_{33}\omega_3^2 \quad (14)$$

$$\omega_1^{i^2}\omega_2^{i^2} + \omega_2^{i^2}\omega_3^{i^2} + \omega_3^{i^2}\omega_1^{i^2} = B_{12}\omega_1^2\omega_2^2 + B_{23}\omega_2^2\omega_3^2 + B_{31}\omega_3^2\omega_1^2 \quad (15)$$

$$\omega_4^{i^2}\omega_5^{i^2} = C_{23}\omega_2^2\omega_3^2 \quad (16)$$

and

$$\omega_4^{i^2} + \omega_5^{i^2} = C_{22}\omega_2^2 + C_{33}\omega_3^2 \quad (17)$$

where the B 's and C 's have the same meaning as in reference [2]. The frequency ω_6 of the B_1 species is calculated from

$$\omega_6^{i^2} = \omega_4^2 \left[\frac{9m_y m_y^i + m_x m_y + 2m_x m_y^i}{3m_y^i(m_x + 3m_y)} \right] \quad (18)$$

The frequencies of the other unsymmetric substitution, $YX_3 \rightarrow XYY_2$ are obtained by simply interchanging m_y and m_y^i in Eqs (13)–(18). The calculated frequencies are given in Table II.

3. Potential energy constants

Using the mixing parameter, the F matrix elements [3] were evaluated from

$$F = \tilde{B}^{-1} A \Lambda AB^{-1} \quad (19)$$

in which Λ is a diagonal matrix whose elements A_k are defined by

$$A_k = 4\pi^2 c^2 \omega_k^2 \quad (20)$$

where c is the velocity of light and ω_k is the vibrational frequency of the k^{th} mode. The B matrix is given as

$$B = UDS_{\text{truncated}} \quad (21)$$

TABLE III

Valence force constants (Mdynes/Å)

Molecule		Present work	Ref. [11]	Ref. [9]	Ref. [15]
NO ₂	f_d	10.667	10.5	10.927	11.043
	f_α	1.126	1.29	1.125	1.109
	f_{dd}	1.769	1.45	2.038	2.140
	$f_{d\alpha}$	0.078	0.098	0.039	0.048
Molecule		Present work	Ref. [10]	Ref. [12]	Ref. [13]
NO ₃ ⁻	f_d	6.734	7.62	8.41	7.62
	f_{dd}	0.940	1.43	0.99	1.40
	$(f_\alpha - f_{\alpha\alpha})$	1.228	1.09	0.90	1.68
	$(f'_{d\alpha} - f'_{d\alpha'})$	-0.812	-0.48	0.74	-0.75
	f_δ	1.503	1.506	1.467	—

where U is the transformation matrix between internal and internal symmetry coordinates, D is the transformation matrix between internal and Cartesian coordinates and S is the transformation matrix between the Cartesian and Cartesian symmetry coordinates. From the potential energy constants obtained from Eq. (19) the valence force constants were deduced and are given in Table III.

4. Mean amplitudes of vibration

The vibrational mean amplitudes were calculated using Cyvin's [4] equation,

$$\Sigma = L\Delta\tilde{L} \quad (22)$$

where

$$\Delta_k = \frac{h}{8\pi^2 c \omega_k} \coth \frac{hc\omega_k}{2KT} \quad (23)$$

and $L = BA$. Here h is Planck's constant, K Boltzmann's constant, c is the velocity of light in vacuum and T is the absolute temperature. The calculated mean vibrational amplitudes are given in Table IV.

TABLE IV

Vibrational mean amplitude (\AA) at 298.16°K

Molecule	Present work	Reference [14]
NO ₂	0.03829	0.0382
NO ₃ ⁻	0.06479	—

5. Coriolis coupling constants

The Coriolis coupling constants, according to Meal and Polo [5] are given in terms of the l matrix as

$$\zeta^\alpha = 1M^\alpha \tilde{l} \quad (24)$$

$\alpha = x, y, z$

where $l = S\tilde{A}$ and M^x , M^y and M^z are as defined in reference [5]. The ζ elements are presented in Table V.

TABLE V

Coriolis coupling constants

Molecule	Zeta element	
NO ₂	ζ_{13}^z	-0.849366
	ζ_{23}^z	0.527844
NO ₃ ⁻	ζ_{24}^z	-0.661569
	ζ_{25}^z	0.183525
	ζ_{34}^z	-0.760405

6. Rotational distortion constants

The rotational distortion parameters for vibration-rotation interaction, given by Wilson and Howard [6] and Nielson [7] are

$$\hbar^4 \tau_{\alpha\beta\gamma\delta} = - \frac{K}{I_{\alpha\alpha}^0 I_{\beta\beta}^0 I_{\gamma\gamma}^0 I_{\delta\delta}^0} \sum_i \frac{a_i^{\alpha\beta} a_i^{\gamma\delta}}{\omega_i^2} \quad (25)$$

where α , β , γ and δ can be in turn x , y or z . If these are expressed in MHZ, the constant K assumes the value 5.7498×10^8 , the vibrational frequencies are in cm^{-1} and the components of the moments of inertia tensor $I_{\alpha\alpha}^0$ evaluated for the ground state and in the centre of mass of the molecule and the coefficients $a_i^{\alpha\beta}$ are expressed in a. m. u. A^0 .

The coefficients $a_i^{\alpha\beta}$ in terms of the l matrix elements and of the equilibrium Cartesian coordinates, α_k , β_k and γ_k , takes the form [8],

$$a_i^{\alpha\alpha} = 2 \sum_k m_k^{1/2} (\beta_k^0 l_{ki}^{\beta\alpha} + \gamma_k^0 l_{ki}^{\gamma\alpha}) \quad (26)$$

$$a_i^{\alpha\beta} = -2 \sum_k m_k^{1/2} \alpha_k^0 \beta_k^0 (\alpha \neq \beta) \quad (27)$$

where m_k is the mass of the k^{th} atom. Following Kivelson and Wilson [16] the centrifugal distortion constants were evaluated, and are given in Table VI.

TABLE VI

Centrifugal distortion constants

Molecule		τ_{xxxx}	τ_{yyyy}	τ_{xxyy}	τ_{xyxy}
$^{14}\text{N}^{16}\text{O}_2$	(Calc.) ^a	-279.6387	-0.044679	-1.859044	-0.24564
	(Obs.) ^b	-299.4	-0.04144	1.843	-0.2453
$^{15}\text{N}^{16}\text{O}_2$	(Calc.)	-241.5574	-0.045813	-1.75338	-0.2338
	(Obs.)	-273.4	-0.04144	1.761	-0.2445
$^{14}\text{NO}_3^-$	(Calc.)	-0.017246	-0.017248	0.017247	-0.0371

a — Present work; b — Reference [15].

7. Discussion

The zero frequencies for $^{14}\text{N}^{16}\text{O}_2$, $^{15}\text{N}^{16}\text{O}_2$, $^{14}\text{N}^{16}\text{O}_2^-$, $^{15}\text{N}^{16}\text{O}_2^-$ and $^{15}\text{N}^{16}\text{O}_3^-$ are given in Table I. As seen in Table II, the frequencies calculated for the isotopic molecules agree well with the observed values [10]. Kato and Rolfe [10] were unable to observe some of the vibrational frequencies both for NO_2^- and NO_3^- . But they have calculated [10] all the frequencies, assuming a most general potential function. Their calculated values are (in cm^{-1})

for $^{15}\text{N}^{18}\text{O}_2^-$: $\omega_1 = 1256.9$ and $\omega_2 = 757.2$

$^{15}\text{N}^{16}\text{O}^{18}\text{O}^-$: $\omega_1 = 1278.9$ and $\omega_2 = 776.8$

$^{14}\text{N}^{18}\text{O}_3^-$: $\omega_3 = 676.4$

$$^{15}\text{N}^{18}\text{O}_3^-: \omega_1 = 994.5, \omega_3 = 675.4 \text{ and } \omega_4 = 808.4$$

$$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-: \omega_3 = 704.8 \text{ and } \omega_6 = 692.8$$

$$^{14}\text{N}^{16}\text{O}^{18}\text{O}_2^-: \omega_3 = 699.8 \text{ and } \omega_5 = 686.1$$

$$^{15}\text{N}^{16}\text{O}_2^{18}\text{O}^-: \omega_1 = 1037.1, \omega_3 = 704.2 \text{ and } \omega_5 = 699.5$$

and $^{15}\text{N}^{16}\text{O}^{18}\text{O}_2^-: \omega_1 = 1014.5, \omega_3 = 684.8, \omega_5 = 691.6 \text{ and } \omega_6 = 812.$

in very close agreement with our calculated values.

The valence force constants for NO_2 were given by Arakawa and Nielson [9] from their infrared study and by Bird *et al.* [15] from a microwave study. Our values are in excellent agreement with those values. The mean amplitude of vibration is comparable with that of Cyvin [14]. The centrifugal distortion constants were evaluated for $^{14}\text{N}^{16}\text{O}_2$, $^{15}\text{N}^{16}\text{O}_2$ and $^{14}\text{N}^{16}\text{O}_3^-$. As seen in Table VI these values are in very good agreement with those observed by Bird *et al.* [15] from their microwave study excepting the τ_{xxy} , for which they observed a positive value. No data are available for comparing Coriolis coupling constants and all the molecular constants agree well with the experimentally observed values, wherever available. Thus Green's function gives a suitable force field for nitrogen-oxygen compounds.

One of the authors (G. S.) is grateful to the University Grants Commission, Government of India, New Delhi for financial assistance by the award of a Junior Research Fellowship.

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