

VIBRATIONAL ISOTOPE EFFECT IN γ SYSTEM OF $^{15}\text{N}^{16}\text{O}$ MOLECULE

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Part of the γ system electronic spectrum of $^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{16}\text{O}$ molecules was obtained with a medium-resolution quartz spectrograph. The isotopic displacements and vibrational constants were obtained for upper and lower states, respectively, from band heads measurements.

$^{15}\text{N}^{16}\text{O}$	$^{14}\text{N}^{16}\text{O}$
$\omega'_e = 2331.0 \pm 1.09 \text{ cm}^{-1}$	$\omega'_e = 2376.08 \pm 1.48 \text{ cm}^{-1}$
$\omega'_e x'_e = 15.77 \pm 0.39 \text{ cm}^{-1}$	$\omega'_e x'_e = 17.07 \pm 0.53 \text{ cm}^{-1}$
$\omega''_e = 1868.84 \pm 0.58 \text{ cm}^{-1}$	$\omega''_e = 1903.35 \pm 0.82 \text{ cm}^{-1}$
$\omega''_e x''_e = 13.47 \pm 0.06 \text{ cm}^{-1}$	$\omega''_e x''_e = 14.11 \pm 0.08 \text{ cm}^{-1}$

The results were compared with those predicted by the simple isotope theory and were found to be in satisfactory agreement.

Introduction

Earlier, Naudé [1] observed the isotope effect in the γ system of the $^{15}\text{N}^{16}\text{O}$ molecule and measured the O—O, O—1, O—2 bands to estimate the natural abundances of $^{15}\text{N}_2$ and $^{18}\text{O}_2$. The determination of the isotopic displacements of band heads and of the approximate vibrational constants for the $A^2\Sigma$ and $X^2\Pi$ states of the $^{15}\text{N}^{16}\text{O}$ molecule is the subject of the present investigation.

The wavelengths of the respective band heads of the $^{14}\text{N}^{16}\text{O}$ molecule were also measured because results obtained by various authors differ [2, 3].

Experimental

The light source was an ordinary discharge tube with a quartz window and aluminium electrodes connected to a high-voltage transformer. The tube was filled with an $\text{N}_2 + \text{O}_2$ mixture (where the nitrogen contained 95% of $^{15}\text{N}_2$), at the total pressure of 2 to 5 mm Hg.

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The spectrum was obtained with a medium-resolution quartz Q — 24 spectrograph (VEB Carl Zeiss, Jena). The reciprocal linear dispersion was 5 to 13 Å/mm, giving a measurement error of about 2.5 cm⁻¹. UV-1 ORWO spectral plates were used and the exposure times were from 1 to 5 minutes. Spark iron lines were used as a standard.

Results

Wave numbers were calculated from the determined wavelengths of the different band heads and arranged in a Deslandres table (Table I). From the relevant differences between horizontal and vertical rows in this table 28 and 16 equations were obtained for constants ω_e and $\omega_e x_e$ of the lower and upper states, respectively. Resolving the equations by means of the least squares method, the vibrational constants and their standard deviations were calculated:

$$\begin{aligned}\omega_e' &= 2331.0 \pm 1.09 \text{ cm}^{-1} & \omega_e' x_e' &= 15.77 \pm 0.39 \text{ cm}^{-1} \\ \omega_e'' &= 1868.84 \pm 0.58 \text{ cm}^{-1} & \omega_e'' x_e'' &= 13.47 \pm 0.06 \text{ cm}^{-1}.\end{aligned}$$

The terms $\omega_e' y_e'$ and $\omega_e'' y_e''$ were neglected because the calculation based on the wave numbers of band heads was not sufficiently exact for their evaluation. The vibrational constants of the ¹⁴N¹⁶O molecule were obtained in the same way:

$$\begin{aligned}\omega_e' &= 2376.08 \pm 1.48 \text{ cm}^{-1} & \omega_e' x_e' &= 17.07 \pm 0.53 \text{ cm}^{-1} \\ \omega_e'' &= 1903.35 \pm 0.82 \text{ cm}^{-1} & \omega_e'' x_e'' &= 14.11 \pm 0.08 \text{ cm}^{-1}.\end{aligned}$$

In order to verify the isotope relations between the constants, the corresponding ratios were calculated:

$$\begin{aligned}(1) \quad & \frac{\omega_e'^i}{\omega_e'} = 0.981 = \varrho_{\text{obs}} & \text{where } \varrho_{\text{calc}} &= \sqrt{\frac{\mu}{\mu^i}} = 0.982 \\ (2) \quad & \frac{\omega_e''^i}{\omega_e''} = 0.982 = \varrho_{\text{obs}} & \text{where } \varrho_{\text{calc}} &= \sqrt{\frac{\mu}{\mu^i}} = 0.982 \\ (3) \quad & \frac{\omega_e'^i x_e'^i}{\omega_e' x_e'} = 0.924 = \varrho_{\text{obs}}^2 & \text{where } \varrho_{\text{calc}}^2 &= \frac{\mu}{\mu^i} = 0.964 \\ (4) \quad & \frac{\omega_e''^i x_e''^i}{\omega_e'' x_e''} = 0.955 = \varrho_{\text{obs}}^2 & \text{where } \varrho_{\text{calc}}^2 &= \frac{\mu}{\mu^i} = 0.964.\end{aligned}$$

The omission of the relatively large constant $\omega_e' y_e'$ (which is 0.28 cm⁻¹ for the ¹⁴N¹⁶O molecule [4]) probably explains the fact that ratio (3) is less exactly equal to ϱ_{calc}^2 .

Considering that the vibrational constants were determined with the use of the mean values of the band heads and not the relevant zero-lines, the agreement between the constants for the ground state and the corresponding results in the infrared [5–7] is satisfactory.

The mean observed isotopic displacement for every band was compared with that

TABLE I

Deslandres table of the $^{15}\text{N}^{18}\text{O}$ bands for wavenumbers band heads of $0P_{12}$, P_2 , P_1 and Q_1 branches with horizontal and vertical differences

v'	v''	0	1	2	3	4	5	6	7
0		44048.92	42208.44	40393.95	38606.25	36846.22	35113.16	33407.05	
		44073.19	42231.08	40415.34	38627.58	36865.24	35131.18	33423.91	
		44173.47	42334.62	40517.06	38728.59	36967.75	35233.82		
		44193.60	42351.83	40535.13	38746.60	36983.61	35250.89		
1		2298.9	2296.9				2300.8	2298.8	
		2299.9					2300.6	2299.9	
		2297.5					2301.0		
		2296.9					2296.9		
2		46347.78	(44505.40)				37414.04	35705.82	34027.99
		46373.15					37431.83	35723.81	34043.06
		46471.01					37534.84	35825.71	
		46490.46					37549.79	35842.67	
			4567.5					2284.18	
			4568.2					2268.50	
			4566.7						
			4567.6						
			44961.47						36291.18
			44983.57						36311.53
			45083.78						(36417.53)
			45102.69						(36431.86)

() blended lines, not used in calculations.

calculated from the formula

$$v^i - v = \omega_e' \left(v' + \frac{1}{2} \right) (\rho - 1) - \omega_e' x_e' \left(v' + \frac{1}{2} \right)^2 (\rho^2 - 1) - \left[\omega_e'' \left(v'' + \frac{1}{2} \right) (\rho - 1) - \omega_e'' x_e'' \left(v'' + \frac{1}{2} \right)^2 (\rho^2 - 1) \right]$$

where determined vibrational constants of the $^{14}\text{N}^{16}\text{O}$ molecule and ρ_{calc} were used (Table II). The agreement between calculated and observed isotope shifts is a proof of the correctness of the present vibrational numbering of the bands.

TABLE II

Isotopic displacements for γ system bands of $^{15}\text{N}^{16}\text{O}$

Band	Isotopic Displacement	
	Observed cm^{-1}	Calculated cm^{-1}
0-0	4.1	4.2
0-1	30.7	29.0
0-2	61.8	61.1
0-3	92.7	92.6
0-4	121.8	122.9
0-5	151.8	152.2
0-6	180.4	180.6
1-0	46.8	45.8
1-5	109.3	110.7
1-7	161.4	166.4
2-2	21.5	20.9
2-7	123.2	126.0

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