

The InfraRed Spectra of N¹⁵N¹⁴O¹⁶ and N¹⁴N¹⁵O¹⁶. Some Thermodynamic Properties of the Isotopic N₂O Molecules

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The molecular frequencies are the same in the spectra of solids (I) and (II), and in the liquid. The frequencies 330, 747, 1071, 1106, and 3072 are found to be polarized in the liquid spectrum and therefore represent the planar vibrations of the molecule, while the frequencies 1573, 1376, 628, and 308 are depolarized. According to Sponer and Kirby-Smith,¹⁷ the latter are the out-of-plane frequencies of the molecule. The different behavior of the planar and the out-of-plane vibrations in the solid is seen in the spectrograms (e) and (f), which represent the spectra taken with the symmetry axis of the crystal along the direction of observation *OY* and the electric vector either along the direction of observation *OY* (spec. e), or along the line perpendicular to the directions of illumination *OX* and of observation *OY* (spec. f). In the former case, the electric vector will lie

in the plane of the molecule. The planar frequencies 747, 1071, 1106, and 3072 are seen to be somewhat weaker in (e) than in (f), while the out-of-plane vibrations 1573, 1376, and 628 show an opposite behavior. This is due to the fact that these planar vibrations are also the totally symmetric vibrations of the molecule, and therefore produce an induced moment in the direction of the electric vector. Since the electric vector is in the direction of observation, they appear weak. The out-of-plane vibrations, on the other hand, give fairly large induced moments perpendicular to the direction of observation, and therefore appear much stronger. The relatively large intensity of the planar vibrations in the spectrogram (e) is due to the fact that they are both symmetric and antisymmetric oscillations for the crystal. (Saksena).¹⁸

¹⁷ H. Sponer and Kirby-Smith, *J. Chem. Phys.* **9**, 667 (1941).

¹⁸ B. D. Saksena, *Proc. Ind. Acad. Sci.* **11**, 229 (1940).

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The Infra-Red Spectra of $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$. Some Thermodynamic Properties of the Isotopic N_2O Molecules*

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The three fundamental frequencies of $N^{15}N^{14}O^{16}$ have been studied in the infra-red. One stretching frequency and the bending frequency in $N^{14}N^{15}O^{16}$ have similarly been investigated. The bending frequencies in $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$ are found to be in good agreement with calculations from the product rule. Some slight changes are made in the force constants for the stretching vibrations in N_2O . The stretching frequency ω_3 in $N^{14}N^{15}O^{16}$ provides a good independent check on the force constants.

The partition function ratios for isotopic exchange reactions involving nitrogen and oxygen in N_2O are calculated. The isomerization equilibrium $N^{15}N^{14}O^{16} = N^{14}N^{15}O^{16}$ has been calculated over the temperature range 273.16°–1000°K. A correlation is drawn between the structures of the isotopic isomers, $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$, and the isomerization equilibrium.

INTRODUCTION

IN the course of an investigation of some aspects of the controlled thermal decomposition of ammonium nitrate into nitrous oxide and water, we prepared a sample of nitrous oxide enriched in N^{15} exclusively in the end position.¹ The availability of such a sample afforded the opportunity of determining its infra-red spectrum with the expectation of improving the potential function for the vibrations of nitrous oxide. In a concurrent and independent investigation, Richardson and Wilson² have described the preparation of a sample of nitrous oxide containing 60 percent N^{15} in the end position and the infra-red spectrum of this molecule in the fluorite and rock salt regions of the spectrum, and have evaluated the stretching force constants in the

potential function

$$2V = f_1 \Delta r_1^2 + f_2 \Delta r_2^2 + 2f_{12} \Delta r_1 \Delta r_2. \quad (1)$$

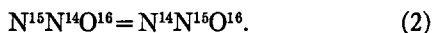
We have measured the shift in the three fundamental vibrational frequencies of N_2O on substitution of N^{15} for N^{14} in the end position and in two of the fundamental vibrations on N^{15} substitution in the center. The measurements on the $N^{14}N^{15}O^{16}$ molecule afford an independent check on the force constants in Eq. (1) and confirm Richardson and Wilson's force constants. A slight improvement of their force constants results from the combination of our measurements on $N^{15}N^{14}O^{16}$ and theirs as evidenced by a better agreement with the product rule and the spectrum of $N^{14}N^{15}O^{16}$. The potential function (1) and the product rule have been used to calculate the vibrational frequencies of $N^{14}N^{14}O^{18}$. From the vibrational frequencies the partition function ratios of the various isotopic N_2O molecules can be calculated. The partition function ratio, f , $N^{14}N^{15}O^{16}/N^{15}N^{14}O^{16}$ is just the equilibrium constant for the

* Research carried out at the Brookhaven National Laboratory under the auspices of the AEC.

¹ L. Friedman and J. Bigeleisen, *J. Chem. Phys.* **18**, 1325 (1950).

² W. S. Richardson and E. B. Wilson, Jr., *J. Chem. Phys.* **18**, 694 (1950).

isomerization equilibrium,



Thus, we can calculate the equilibrium between a pair of isotopic isomers. The results of the measurements and calculations are presented below.

EXPERIMENTAL

The preparation of a sample containing 7.5 percent N¹⁵ in the end position has been described previously.¹ A sample of N₂O containing 31.4 percent N¹⁵ in the center position and 0.4 percent N¹⁵ in the end position was prepared from 31.4 percent N¹⁵—HNO₃ as a starting material. The nitric acid was obtained from the Eastman Kodak Company. Five millimoles of the enriched nitric acid were titrated with ordinary ammonium hydroxide to the stoichiometric end point; brom-phenol blue was used as an external indicator. The solution was evaporated to dryness and the solid ammonium nitrate was decomposed to give N₂O by the method described previously.¹ It has been shown^{1,2} that the decomposition of N¹⁵H₄N¹⁴O₃ yields N¹⁵N¹⁴O exclusively. Therefore, the decomposition of a sample of ammonium nitrate enriched in N¹⁵ in the nitrate ion yields N₂O enriched in N¹⁵ in the middle position.

The spectra were measured with a Baird Associates, Inc., Model B infra-red recording spectrophotometer. The shifts in the ν_1 and ν_3 bands, 1285.4 and 2224.1 cm⁻¹, respectively, in N¹⁴N¹⁴O¹⁶, were measured with a rock salt prism; those in the ν_2 band were measured with a KBr prism. The cells were 5 cm long and equipped with KBr windows. A sample of tank N₂O was used in the reference cell. The shifts were measured from experiments in which the pressure in the reference cell was equal to the total pressure of N₂O in the sample cell. The shutter in front of the mirror in the sample beam was adjusted to give roughly 50 percent transmittance in a spectral region of no absorption. Under these conditions an excess transmittance, negative absorption, appears at the absorption frequencies of N¹⁴N¹⁴O¹⁶ corresponding to the amount of absorption for one of the N¹⁵ substituted molecules at its corresponding frequency. This negative absorption provides an internal wave-length calibration of the instrument. The wave-length shift was determined using the dispersion of the instrument as furnished by the manufacturer. The frequency shift over a small spectral region is given by the relation

$$\Delta\nu = -\bar{\nu}^2\Delta\lambda, \quad (3)$$

where $\bar{\nu}$ is the average of the frequency determined by Plyler and Barker³ and the corresponding N¹⁵ substituted frequency and is easily calculated to a higher precision than the present experimental measurements. Determinations of the wave-length shifts were made by measurements of recorded spectra as well as point-by-

TABLE I. Frequency shifts on N¹⁵ substitution in N₂O (cm⁻¹).

Designation	N ¹⁴ N ¹⁴ O ¹⁶ ^a	N ¹⁴ N ¹⁴ O ¹⁶ — N ¹⁵ N ¹⁴ O ¹⁶ ^b	N ¹⁴ N ¹⁴ O ¹⁶ — N ¹⁵ N ¹⁴ O ¹⁶	N ¹⁴ N ¹⁴ O ¹⁶ — N ¹⁴ N ¹⁵ O ¹⁶
ν_1	1285.0	17.5	16.1 ± 1.4	...
ν_2	588.8	...	4.2 ± 0.3	12.9 ± 0.2
ν_3	2223.5	22.5	29 ± 4	46.5 ± 2.0

^a Measurements of Plyler and Barker (reference 3) reduced to vacuum (reference 6).

^b W. S. Richardson and E. B. Wilson (reference 2).

point manual scanning of the spectrum. The latter gave better precision and reproducibility because of the fact that the response time of the bolometer and recording system is not negligible in comparison with the time to scan an absorption peak.

The above procedure for measuring small frequency shifts was checked by measurement of the separation of close absorption lines in the ammonia spectrum. The separations measured in this way were compared with the precise grating measurements of Barker.⁴ No systematic deviations were found and the accuracy of our determinations was limited by the precision to which the wave-length shift could be measured. The corresponding errors in the shifts in the N₂O spectrum on N¹⁵ substitution are indicated along with the experimental results.

RESULTS

The shifts in the bending frequency, ν_2 , were easily resolved by the KBr optics and were determined from the separation of the pronounced Q branches. In accord with expectations no shift could be found in the low stretching frequency, ν_1 , for the N¹⁴N¹⁵O¹⁶ molecule. In the case of the N¹⁵N¹⁴O¹⁶ molecule the shifts in ν_1 in both the P and R branches were clearly resolved and measured. In the measurements of the ν_3 shift in N¹⁵N¹⁴O¹⁶ the R branch of the N¹⁵N¹⁴O¹⁶ molecule was completely unresolved from the P branch of the N¹⁴N¹⁴O¹⁶. The separation between the R branch of N¹⁴N¹⁴O¹⁶ and the P branch of N¹⁵N¹⁴O¹⁶ was measured. The shift in the band origin was calculated from this measured separation and the value of 28 cm⁻¹ estimated for the P—R separation.^{3,5} The shift in ν_3 in the N¹⁴N¹⁵O¹⁶ molecule was sufficiently large so that the P and R branches of both the N¹⁴N¹⁴O¹⁶ and N¹⁴N¹⁵O¹⁶ molecules appeared distinctly. The experimentally determined frequency shifts are given in Table I.

The shifts determined for the N¹⁵N¹⁴O¹⁶ agree with the measurements made by Richardson and Wilson within the limits of the experimental errors of both measurements. As will be shown below, their shift in ν_3 is undoubtedly more accurate than ours as a result of their use of a fluorite prism to measure this shift.

The experimental zero-order stretching frequencies are tabulated in Table II. The zero-order frequencies

⁴ E. F. Barker, Phys. Rev. **55**, 657 (1939).

⁵ C. P. Snow, Proc. Roy. Soc. **A128**, 294 (1930).

¹ E. K. Plyler and E. F. Barker, Phys. Rev. **38**, 1827 (1931).

TABLE II. Zero-order stretching frequencies for the isotopic N₂O molecules (cm⁻¹).

Molecule		N ¹⁴ N ¹⁴ O ¹⁶			N ¹⁵ N ¹⁴ O ¹⁶			N ¹⁴ N ¹⁵ O ¹⁶			N ¹⁴ N ¹⁴ O ¹⁸
Designation	Observed	Calculated from force constants A, Table IV	Calculated from force constants C, Table IV	Observed R+W	Observed this research	Calculated from force constants A, Table IV	Calculated from force constants C, Table IV	Observed	Calculated from force constants A, Table IV	Calculated from force constants C, Table IV	Calculated from force constants C, Table IV
ω ₁	1299.8	1298.8	1299.8	1281.9	1283.3	1283.0	1283.5	—	1296.2	1297.6	1256.2
ω ₃	2276.5	2277.1	2276.5	2252.9	2246.2	2252.3	2252.6	2227.8	2228.8	2228.1	2270.8

TABLE III. Zero-order bending frequencies for the isotopic N₂O molecules (cm⁻¹).

Molecule	ω ₂ observed	ω ₂ calculated (product rule)
N ¹⁴ N ¹⁴ O ¹⁶	596.5	...
N ¹⁶ N ¹⁴ O ¹⁶	592.2	592.9
N ¹⁴ N ¹⁵ O ¹⁶	583.2	582.8
N ¹⁴ N ¹⁴ O ¹⁸	...	591.9

TABLE IV. Force constants^a and product rule check for the stretching frequencies in N₂O.

Quantity	A Richardson and Wilson	B N ¹⁵ N ¹⁴ O ¹⁶ (this research)	C See below ^b	Product rule
f ₁	18.98	22.22	18.71 ₇	
f ₂	11.50	10.31	11.61 ₁	
f ₁₂	1.43	3.56	1.312 ₇	
ω ₁ ω ₃ /ω ₁ ⁱ ω ₃ ⁱ	1.0246	1.0265	1.0240	1.0235

^a Force constants in units of 10⁵ dynes/cm.^b Calculated from ω₃(N¹⁵N¹⁴O¹⁶) from Richardson and Wilson and ω₁(N¹⁵N¹⁴O¹⁶) from the average of R and W and this research.

for N¹⁴N¹⁴O¹⁶ are those calculated by Herzberg⁶ from the observed fundamentals, combination and overtone bands. The zero-order frequencies for N¹⁵N¹⁴O¹⁶ and N¹⁴N¹⁵O¹⁶ have been calculated from the ones for N¹⁴N¹⁴O¹⁶, the observed shifts in Table I, and the approximate relations introduced by Dennison,⁷

$$\omega_j = \nu_j(1 + \alpha_j), \quad (4)$$

$$\omega_j^i \simeq \nu_j^i [1 + \alpha_j(\nu_j^i/\nu_j)]. \quad (5)$$

The zero-order bending frequencies are given in Table III.

The first check that can be made on the isotopic zero-order frequencies is by means of the Teller-Redlich product rule.⁸ For the linear XYZ molecule the rule states

$$\omega_1\omega_3/\omega_1^i\omega_3^i = (m^iM/mM^i)^{\frac{1}{2}}, \quad (6)$$

$$\omega_2/\omega_2^i = (m^iMI/mM^iI^i)^{\frac{1}{2}}, \quad (7)$$

where the superscript *i* refers to the isotopically substituted molecule, *m* is the mass of the isotopically substituted atom, *M* is the mass of the molecule, and *I* is the moment of inertia of the molecule. The bending vibrations ω₂^{*i*} have been calculated from Eq. (7) with the value of ω₂ calculated from Plyler and Barker's data.⁶ The moments of inertia of N¹⁴N¹⁴O¹⁶, N¹⁵N¹⁴O¹⁶, and N¹⁴N¹⁵O¹⁶ have been determined by microwave spectroscopy.^{9,10} The experimentally determined microwave frequencies were used directly, since *I*α₁/ν. The moment of inertia of N¹⁴N¹⁴O¹⁸ was calculated using 1.126 Å and 1.191 Å for the N—N and N—O bond distances,⁹ respectively. The values of ω₂ calculated from the product rule are compared with experiment in Table III. The agreement between the observed and

calculated frequencies is satisfactory. The deviations can be ascribed to experimental error and the reduction of the observed frequencies to zero-order frequencies by Dennison's approximation.

The product rule check for the stretching frequencies is given in Table IV. It is clear from the product rule check that Richardson and Wilson's value for ω₃ for N¹⁵N¹⁴O¹⁶ is to be preferred to ours. The best agreement with the product rule is obtained by using their value for ω₃ and our value for ω₁ for N¹⁵N¹⁴O¹⁶, together with Plyler and Barker's measurements on N¹⁴N¹⁴O¹⁶. This combination gives for the ratio of the product of the stretching frequencies 1.0235, in perfect agreement with the product rule. There is no other reason to prefer our measurements for ω₁ over those of Richardson and Wilson. Therefore, we have chosen as the best set of values for the zero-order frequencies for N¹⁵N¹⁴O¹⁶ their value for ω₃ and the average of their value and ours for ω₁.

The force constants in the potential function (1) can be calculated from the zero-order frequencies by the use of the following relations:

$$\lambda_1 + \lambda_3 = (\mu_x + \mu_y)f_1 + (\mu_y + \mu_z)f_2 - 2\mu_yf_{12}, \quad (8)$$

$$\lambda_1\lambda_3 = (\mu_x\mu_y + \mu_x\mu_z + \mu_y\mu_z)(f_1f_2 - f_{12}^2), \quad (9)$$

where λ = 4π²ω² and μ_{*k*} = 1/*m_k*. Equations (8) and (9) have been solved for the force constants from the zero-order frequencies of N¹⁴N¹⁴O¹⁶ and N¹⁵N¹⁴O¹⁶. Three sets of force constants are listed in Table IV corresponding to three sets of frequencies for N¹⁵N¹⁴O¹⁶. The force constants in column A are those calculated by Richardson and Wilson; those in column B are calculated from our measurements on N¹⁵N¹⁴O¹⁶; those in column C are calculated from Richardson and Wilson's value for ω₃ and the average of their value and ours for ω₁. Our value of ω₃ leads to an unsatisfactory set of force constants. The resulting value of *f*₁, corresponding to N—N

⁶ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 278.

⁷ D. M. Dennison, *Rev. Mod. Phys.* **12**, 175 (1940).

⁸ See reference 6, pp. 112, 231 ff.

⁹ Coles, Elyash, and Gorman, *Phys. Rev.* **72**, 973 (1947).

¹⁰ D. K. Coles, and R. H. Hughes, *Phys. Rev.* **76**, 178 (1949).

stretching, is higher than the force constant in the nitrogen molecule, which seems unreasonable. The interaction constant, f_{12} , is also rather large. There is little difference between the force constants in column *C* and those in column *A*. As has been pointed out by Richardson and Wilson, the interaction constant is most sensitive even to the slight changes which we have introduced in Richardson and Wilson's values for the frequency shifts.

The stretching frequencies in the molecules N¹⁴N¹⁴O¹⁶, N¹⁵N¹⁴O¹⁶, N¹⁴N¹⁵O¹⁶, and N¹⁴N¹⁴O¹⁸ have been calculated from the force constants in Table IV. They are compared with experiment in Table II. The only independent check on the force constants is afforded by the measured value of ω_3 for N¹⁴N¹⁵O¹⁶. The agreement of both force constant sets *A* and *C* is well within the limits of the experimental error. Set *C* gives a slightly better agreement than does set *A*. Either set of force constants can be used to calculate the stretching frequencies of any one of the isotopic N₂O molecules to a few tenths of a wave number.

THERMODYNAMIC PROPERTIES

The vibrational frequencies for N¹⁴N¹⁴O¹⁶, N¹⁵N¹⁴O¹⁶, N¹⁴N¹⁵O¹⁶, and N¹⁴N¹⁴O¹⁸ in Tables II and III can be used to calculate nitrogen and oxygen exchange equilibria involving N₂O. The equilibria are most readily calculated with the aid of the tables published for calculating partition function ratios.¹¹ The partition function ratios, f values,¹¹ for nitrogen and oxygen substitution in N₂O are given in Table V. The stretching frequencies used in the calculations were those calculated from force constants *C* in Table IV, the bending frequencies were those calculated in Table III. The conversion factor, hc/k , was taken as 1.43847.¹²

The partition function ratio, f , N¹⁴N¹⁵O¹⁶/N¹⁵N¹⁴O¹⁶, is the equilibrium constant for the isomerization reaction (2). This can readily be seen from the definition of f .¹³ The values for this equilibrium constant are about as large as most of the ones which arise from the exchange of nitrogen atoms between different chemical species.¹⁴ This may appear surprising and counter to the expectation that isotopic isomerization equilibrium constants

TABLE V. Partition function ratios and exchange equilibria involving N₂O.

T°K	f N ¹⁵ N ¹⁴ O ¹⁶ N ¹⁴ N ¹⁴ O ¹⁶	f N ¹⁴ N ¹⁵ O ¹⁶ N ¹⁴ N ¹⁴ O ¹⁶	$f=K$ N ¹⁴ N ¹⁵ O ¹⁶ N ¹⁵ N ¹⁴ O ¹⁶	f N ¹⁴ N ¹⁴ O ¹⁸ N ¹⁴ N ¹⁴ O ¹⁶	K N ¹⁴ N ¹⁴ O ¹⁸ H ₂ O ¹⁶ N ¹⁴ N ¹⁴ N ¹⁶ H ₂ O ¹⁸
273.16	1.0911	1.1420	1.0467	1.1127	1.0359
298.16	1.0811	1.1262	1.0417	1.0916	1.0233
300	1.0805	1.1252	1.0414	1.0908	
400	1.0539	1.0838	1.0284	1.0586	1.0116
500	1.0386	1.0603	1.0209	1.0408	1.0056
600	1.0290	1.0454	1.0159	1.0299	1.0023
700	1.0225	1.0354	1.0126	1.0227	
800	1.0179	1.0283	1.0102	1.0179	
900	1.0146	1.0232	1.0085	1.0144	
1000	1.0122	1.0192	1.0069	1.0118	

should be smaller than equilibrium constants for exchange between different kinds of molecules. The large equilibrium constant in the present case can be understood from the nature of the normal modes of vibration and the product rule. The shift in the stretching frequencies on N¹⁵ substitution is distributed between the modes corresponding to ω_1 and ω_3 . In the mode ω_1 the central nitrogen atom is virtually at rest; and, therefore, N¹⁵ substitution in the central position puts almost all of the shift in the high frequency ω_3 . This makes a large contribution to f by virtue of the larger values of both the factor $G(u)$ and also Δu . The bending mode, which is doubly degenerate, also has a larger shift on N¹⁵ substitution in the center rather than on the end because of the fact that the center atom is very close to the center of gravity of the molecule.

The oxygen exchange equilibrium constant between gaseous N₂O and H₂O is also included in Table V. The partition function ratios for the water molecules are taken from Urey's tabulation.¹⁴ This equilibrium has been calculated previously by Rosenthal,¹⁵ who obtained the value 1.056 at 0°C. The discrepancy between Rosenthal's calculations and those in Table V arises from the fact that her stretching frequencies for N¹⁴N¹⁴O¹⁸ were calculated from a potential function based entirely on the spectrum of N¹⁴N¹⁴O¹⁶.

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We wish to thank Mr. W. S. Richardson and Professor E. B. Wilson, Jr. for sending us a copy of their manuscript on the infra-red spectrum of N¹⁵N¹⁴O prior to publication.

¹⁵ J. E. Rosenthal, J. Chem. Phys. 5, 465 (1937).

¹¹ J. Bigeleisen and M. G. Mayer, J. Chem. Phys. 15, 261 (1947). See Eq. (11a) and Table I.

¹² "Selected values of chemical thermodynamic properties" (Nat. Bur. Stand., June 30, 1948).

¹³ See Eq. (7), reference 11.

¹⁴ H. C. Urey, J. Chem. Soc. 1947, 562.