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Microwave Spectrum and Molecular Constants of Nitrosyl Bromide*

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The microwave spectrum of NOBr has been studied in the region 20 000 to 40 000 Mc/sec and an analysis made of the $J=2 \rightarrow 3$ transition. The following molecular constants were obtained.

	NOBr ⁷⁹	NOBr ⁸¹
Rotational constants (Mc/sec)		
A	83 340	83 340
B	3747.24	3722.49
C	3586.00	3563.34
Asymmetry parameter b	-0.001012	-0.000998
Quadrupole coupling components (Mc/sec)		
χ_{aa}	388.3	325.5
χ_{bb}	-239.5	-200.2
χ_{cc}	-148.8	-125.3

The structural parameters obtained from these are $d(\text{N}-\text{O})=1.15$ A, $d(\text{N}-\text{Br})=2.14$ A, $d(\text{O}-\text{Br})=2.81$ A, and $\angle \text{Br}-\text{N}-\text{O}=114^\circ$. The interatomic distances are compared with electron diffraction results, and a brief interpretation of the quadrupole coupling in terms of chemical bonds is given.

INTRODUCTION

THE internuclear distances and bond angle of nitrosyl bromide have been measured by electron diffraction. J. A. Ketelaar and K. J. Palmer¹ report the values $d(\text{N}-\text{Br})=2.14 \pm 0.02$ A, $d(\text{N}-\text{O})=1.15 \pm 0.04$ A, $d(\text{O}-\text{Br})=2.85 \pm 0.02$ A, and $\angle \text{Br}-\text{N}-\text{O}=117^\circ \pm 3^\circ$. The moments of inertia for NOBr⁸¹ calculated from this structure are $I_A=9.39 \times 10^{-40}$ g cm², $I_B=230 \times 10^{-40}$ g cm² and $I_C=240 \times 10^{-40}$ g cm², indicating that the molecule is an almost symmetric top. The rotational spectrum predicted on the basis of these moments consists of three groups of lines centered at approximately 21 400, 28 500, and 35 700 Mc/sec for the $J=2 \rightarrow 3$, $3 \rightarrow 4$, and $4 \rightarrow 5$ transitions, respectively. Similarly the predicted spectrum for NOBr⁷⁹ in this region consists of three groups of lines which overlap the corresponding groups of NOBr⁸¹. The observed lines fall into groups 400 to 700 Mc/sec higher in frequency than those predicted. This rough agreement between the observed and calculated spectra served as a preliminary identification of the J values involved in each transition. The observed spectrum is difficult to interpret due to the asymmetry of the molecule, the large quadrupole moments of the bromine nuclei, the presence of two isotopic species, and a complicated Stark effect. The present analysis is based primarily on the $J=2 \rightarrow 3$ transition.

EXPERIMENTAL

The sample of NOBr was prepared by admitting gaseous NO and Br₂ in the ratio 2 to 1 to a 1000 cc flask until a final pressure of 1 atmosphere was obtained. The mixture was then frozen with liquid nitrogen, and the excess NO was pumped off. The NOBr was given off the remaining solid as its temperature was increased. This sample was allowed to flow through an absorption cell cooled to dry ice temperature.

The absorption lines were observed on the oscilloscope of a Stark modulated microwave spectrograph. The absorption cell consisted of X-band wave guide 18 ft long with a brass strip mounted in the center as first described by Hughes and Wilson.² The Stark voltage was an 85 kc square wave of variable amplitude but zero-based so that one side of the square wave was held at ground potential. Frequencies were measured using a microwave frequency standard built by Scientific Associates of Atlanta, Georgia. It employs a 5 Mc/sec crystal controlled oscillator which may be zero-beat against the 5 or 10 Mc/sec signal from station WWV. The oscillator frequency is multiplied by vacuum tube circuits up to 2160 Mc/sec and multiplied by a 1N26 silicon crystal to the microwave region. The frequency measurements were made in the manner described by Unterberger and Smith³ with the exception that they were made in pairs by first sweeping the klystron from low to high frequency and then reversing

* Sponsored by the Office of Ordnance Research, U. S. Army.

¹ J. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).

² R. H. Hughes and E. B. Wilson, Phys. Rev. **71**, 562 (1947).

³ R. R. Unterberger and W. V. Smith, Rev. Sci. Instr. **19**, 580 (1948).

TABLE I. Calculated and observed frequencies (Mc/sec) of the $J=2 \rightarrow 3$ transition of NOBr. The estimated errors of the observed frequencies are 0.25 Mc/sec.

J	Transition F	Calculated freq.	NOBr ⁷⁹ Weighted average ^a	Observed freq.	Calculated freq.	NOBr ⁸¹ Weighted average ^a	Observed freq.
$2_{-1} - 3_{-2}$	5/2-5/2	21 743.36		21 742.93	21 606.47		21 606.22
	1/2-3/2	21 745.67		21 745.74	21 608.51		21 608.49
	7/2-9/2	21 747.78		21 747.91	21 610.24		21 609.91
	3/2-5/2	21 769.93		21 769.84	21 628.84		21 628.84
	5/2-7/2	21 772.04		21 771.95	21 630.58		21 630.32
$2_{-2} - 3_{-3}$	5/2-7/2	21 994.15	21 994.17	21 993.86	21 852.62	21 852.64	21 852.23
	7/2-9/2	21 994.18			21 852.65		
	3/2-5/2	22 018.19	22 018.21	22 016.97	21 872.77	21 872.78	21 871.10
	1/2-3/2	22 018.23			21 872.80		
$2_1 - 3_0$	7/2-9/2	21 972.00	21 973.03	21 972.29	21 834.22	21 834.70	21 835.19
	7/2-7/2	21 972.00			21 834.22		
	7/2-5/2	21 972.00			21 834.22		
$2_2 - 3_1$	7/2-9/2	21 972.94			21 835.17		
	7/2-7/2	21 973.00			21 835.22		
	7/2-5/2	21 972.97			21 835.20		
$2_1 - 3_0$	3/2-3/2	21 994.74	22 000.21	22 001.07	21 857.47	21 857.95	21 858.69
	3/2-5/2	21 999.74			21 857.47		
$2_2 - 3_1$	3/2-3/2	22 000.64			21 858.39		
	3/2-5/2	22 000.70			21 858.44		
$2_1 - 3_0$	5/2-3/2	22 069.08	22 069.56	22 069.77	21 915.59	21 916.08	21 916.77
	5/2-5/2	22 069.08			21 915.59		
	5/2-7/2	22 069.08			21 915.59		
$2_2 - 3_1$	5/2-3/2	22 069.97			21 916.50		
	5/2-5/2	22 070.03			21 916.54		
	5/2-7/2	22 070.05			21 916.57		
$2_0 - 3_{-1}$	7/2-9/2	22 230.43		22 230.38	22 086.79		22 086.65
	1/2-3/2	22 233.93		22 233.60	22 089.69		22 089.42
	5/2-7/2	22 254.69		22 254.57	22 107.12		22 106.69
	3/2-5/2	22 258.20		22 258.34	22 110.03		22 110.25

^a The calculated relative intensities were used for the weighting factors.

the sweep voltage. The average of the two measurements was taken as the line frequency.

ANALYSIS OF DATA

The observed and computed line frequencies are listed in Table I. The value of F in this table is obtained by the addition of the rotational quantum number J and the spin $I=3/2$ of the bromine nucleus. The small quadrupole interaction of the nitrogen nucleus was expected to produce splittings of less than 1 Mc/sec and has been neglected. The rotational spectrum of NOBr for the $J=2 \rightarrow 3$ transition consists of five lines for each isotopic species as shown in Fig. 1. Each of these lines is split into several components by the large bromine nuclear quadrupole interaction with the electric field gradient at the bromine nucleus giving the 28 lines of observable intensity listed in Table I.

The quadrupole splitting of the observed lines was calculated by the first-order theory of Bragg.⁴ For the

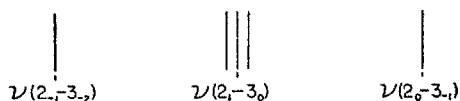


FIG. 1. Pure rotational spectrum for the $J=2 \rightarrow 3$ transition of NOBr⁷⁹.

⁴ J. K. Bragg, Phys. Rev. 74, 533 (1948).

initial calculations the electron distribution near the bromine nucleus was assumed to be symmetric about the N-Br bond axis. This resulted in a predicted spectrum in fairly close agreement with that observed, and the coupling constants reported previously.⁵ Later measurements revealed the splitting of the $2_{-1} \rightarrow 3_{-2}$ and $2_0 \rightarrow 3_{-1}$ lines shown in Table I and made possible a calculation of the diagonal components of the quadrupole coupling tensor with respect to the molecular principal axes. Bragg's theory was applied first by the use of his Eq. (8) and the tabulated line intensities of Cross, Hainer, and King⁶ making a linear interpolation. Because of the coarseness of the table of line intensities a second calculation was made using Bragg's equation (10) and the expansion coefficients $S_{K\tau}$ computed for a rotator with asymmetry parameter $b=10^{-3}$. The difference in the spectra calculated by the two methods was almost insignificant. The spectrum predicted by the latter method is recorded in Table I. The coupling constants computed from the observed spectrum are listed in Table II, where $\chi_{aa}=eQ(\partial^2 V/\partial a^2)$, $\chi_{bb}=eQ(\partial^2 V/\partial b^2)$, and $\chi_{cc}=eQ(\partial^2 V/\partial c^2)$.

⁵ Quitman Williams and T. L. Weatherly, Phys. Rev. 98, 1159(A) (1955).

⁶ Cross, Hainer, and King, J. Chem. Phys. 12, 210 (1944).

From the observed spectrum and the calculated quadrupole splittings the rotational spectrum without quadrupole splitting was determined. The rotational constants were then calculated by the theory of Wang.⁷ According to this theory the rotational energies of the asymmetric top molecule are given by

$$F(J_r) = \frac{1}{2}(B+C)J(J+1) + [A - \frac{1}{2}(B+C)]W_r, \quad (1)$$

where A , B , and C are the rotational constants, and J is the rotational quantum number. The $2J+1$ values of W_r are obtained as solutions to algebraic equations in terms of the asymmetry parameter

$$b = -\frac{\frac{1}{2}(B-C)}{[A - \frac{1}{2}(B+C)]}.$$

For NOBr, b is approximately 10^{-3} , and it is convenient to expand the values of W_r in terms of b . The values of W_r which are important to this analysis are:

$$\begin{aligned} \text{for } J=2 & & \text{for } J=3 \\ W_{+1}=4 & & W_0=4 \\ W_0=1-3b & & W_{-1}=1-6b-\frac{15}{8}b^2+\frac{45}{32}b^3+\dots \\ W_{-1}=1+3b & & W_{-2}=1+6b-\frac{15}{8}b^2-\frac{45}{32}b^3+\dots \end{aligned}$$

These values of W_r when substituted into Eq. (1) give

TABLE II. Bromine quadrupole coupling constants.

	Br ⁷⁹	Br ⁸¹
χ_{aa}	388.3 ± 2.9 Mc/sec	325.5 ± 2.9 Mc/sec
χ_{bb}	-239.5 ± 3.6	-200.2 ± 3.6
χ_{cc}	-148.8 ± 6.5	-125.3 ± 6.5

for the frequency of the center line of Fig. 1

$$\nu(2_{+1} \rightarrow 3_0) = 3(B+C)$$

and for the frequency difference between the upper and lower lines

$$\nu(2_0 \rightarrow 3_{-1}) - \nu(2_{-1} \rightarrow 3_{-2}) = 3(B-C) \left[1 - \frac{15}{32}b^2 + \dots \right].$$

Since b^2 is approximately 10^{-6} this term and all higher order terms of the last equation may be neglected and approximate values of the rotational constants B and C may be determined from the three lines identified in Fig. 1. The approximate values of B and C were then adjusted slightly to obtain the best fit of observed and calculated spectra. The resulting rotational constants are listed in Table III. The constant A in this table was determined from the relation $I_C = I_A + I_B$ for

⁷ S. C. Wang, Phys. Rev. **34**, 243 (1929).

TABLE III. Rotational constants for NOBr.

	NOBr ⁷⁹	NOBr ⁸¹
A	$83\,340 \pm 104$ Mc/sec	$83\,340 \pm 117$ Mc/sec
B	3747.24 ± 0.10	3722.49 ± 0.11
C	3586.00 ± 0.10	3563.34 ± 0.11
Asymmetry parameter b	-0.001012	-0.000998

a planar molecule. Although this relationship is not entirely accurate for a vibrating molecule the error introduced should be small compared to the limits placed on this constant in Table III.

The rotational constants of two isotopic species of NOBr along with a knowledge of the general shape of the molecule provide more than enough data for computing the structure. In order to make use of all the data the structural parameters were calculated by two different methods which prove to be almost independent. The first has been described by J. Kraitchman⁸ and makes use of the moments of inertia I_A^{79} , I_B^{79} , I_A^{81} , and I_B^{81} , the factor of major importance being the difference $I_B^{81} - I_B^{79}$.

A second solution utilizing different data may be obtained by computing the momental dyadic in terms of a , b , c , and θ of Fig. 2 and transforming to principal axes. From the secular determinant one obtains the equations

$$\begin{aligned} I_C &= (m_2 m_3 a^2 + m_1 m_3 b^2 + m_1 m_2 c^2) / M, \\ I_A I_B &= m_1 m_2 m_3 a^2 c^2 \sin^2 \theta / M, \end{aligned}$$

where m_i are the respective masses and M is the total mass. By applying the above equations to each isotopic species one gets for the structural constants of Fig. 2

$$\begin{aligned} a^2 &= \frac{m_1' M I_C - m_1 M' I_C'}{(m_1' - m_1) m_2 m_3}, \\ g^2 &= \frac{M' M (I_C' - I_C)}{(m_2 + m_3)^2 (m_1' - m_1)}, \\ \sin^2 \phi &= \frac{M I_A I_B}{m_1 m_2 m_3 a^2 g^2}, \end{aligned}$$

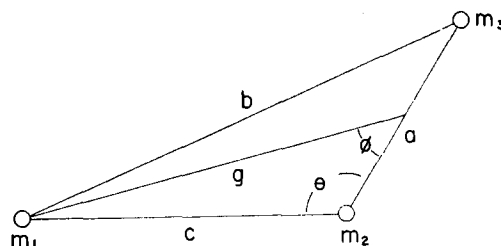


FIG. 2. Parameters used in determining the molecular structure. The line g joins m_1 with the center of mass of m_2 and m_3 .

⁸ J. Kraitchman, Am. J. Phys. **21**, 17 (1953).

TABLE IV. Structure of NOBr from microwave data.

$d(\text{N}-\text{O}) = 1.15 \pm 0.06 \text{ \AA}$
$d(\text{N}-\text{Br}) = 2.14 \pm 0.06 \text{ \AA}$
$d(\text{Br}-\text{O}) = 2.81 \pm 0.04 \text{ \AA}$
$\angle \text{Br}-\text{N}-\text{O} = 114^\circ$

where a is the distance between atoms 2 and 3, g is the distance from 1 to the center of mass of 2 and 3, and ϕ is the angle between g and a . Isotopic substitution is made for atom 1 and the primed quantities refer to the molecule containing the heavier isotope. The bond distances and angle may be obtained from a , g , and ϕ by the laws of trigonometry. The values of a , b , c , and θ obtained by this method depend on I_A^{79} , I_B^{79} , I_C^{79} , and I_C^{81} with I_C^{79} and I_C^{81} having the greatest influence on the results.

Since the accuracy of the first method depends on a precise measurement of I_B^{79} and I_B^{81} and the accuracy of the second method depends on a precise measurement of I_C^{79} and I_C^{81} both methods were used for determining a , b , and c . The results of the two methods agreed to within 0.01 Å for all distances. The average values obtained by the two methods are recorded in Table IV.

RESULTS

The observed lines in Table I varied in width from 1 to 3 Mc/sec. Calculated lines separated by less than 1 Mc/sec have been weighted according to their relative intensities and averaged. In most cases this weighted average agrees with the observed line to within less than 0.5 Mc/sec, the most notable exceptions being the $2_{-2} \rightarrow 3_{-3}$ transition in each molecule. These lines, unlike the others, require a very high Stark voltage for detection, and it seems likely that they were displaced to lower frequencies by incompletely-separated Stark components.

The structural parameters listed in Table IV differ from the electron diffraction results only in the O—Br distance and the bond angle. Unfortunately the present analysis does not give structural constants as accurately as electron diffraction. The geometry of the molecule is such that a change in one distance can be compensated by proper adjustment of the two remaining distances with very little effect on the spectrum. However, if $d(\text{N}-\text{O}) = 1.15 \text{ \AA}$ and $d(\text{N}-\text{Br}) = 2.14 \text{ \AA}$ as measured by electron diffraction and calculated from the spectrum, then $d(\text{O}-\text{Br})$ must be less than 2.83 Å. Therefore it would seem that the electron diffraction measurement of this distance is a little large.

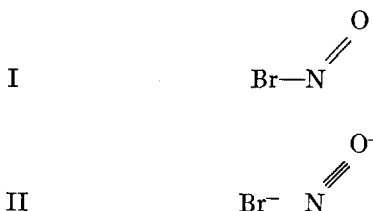
The ratio of the Br^{79} to Br^{81} quadrupole coupling components from Table II is 1.193 ± 0.020 for the components χ_{aa} and 1.196 ± 0.040 for the components χ_{bb} . These ratios are in good agreement with coupling constant ratios obtained from pure quadrupole resonance in solid bromine compounds.

In order to increase the usefulness of the bromine quadrupole coupling tensor for analysis of the N—Br bond it has been transformed to a coordinate system with z axis oriented along the bond direction, x axis in the plane of the molecule and y axis perpendicular to this plane. Such a transformation requires the knowledge of the component χ_{ab} as well as the diagonal elements listed in Table II. Goldstein⁹ has pointed out that this off-diagonal element may be computed if we assume that the xyz axes are principal axes of the quadrupole coupling tensor. Following this suggestion the value of χ_{xy} obtained from the tensor transformation was set equal to zero and the resulting equation solved for χ_{ab} . The transformation to xyz axes was then made in the usual way. The diagonal elements in Mc/sec with respect to this set of axes are

	NOBr ⁷⁹	NOBr ⁸¹
χ_{xx}	−290.2	−242.6
χ_{yy}	−148.8	−125.3
χ_{zz}	+439.0	+367.9

The asymmetry parameter $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ is −0.322 for NOBr⁷⁹ and −0.319 for NOBr⁸¹.

Ketelaar and Palmer¹ have suggested for NOBr the two structures



each making a 50% contribution. The second of these was introduced to explain the large N—Br distance of 2.14 Å compared to a sum of covalent radii 1.84 Å. The large asymmetry parameter $\eta \approx -0.320$ suggests an appreciable contribution of a third structure,



The importance of this structure in bond formation is related to the quantity

$$\delta = \frac{\chi_{xx} - \chi_{yy}}{-(3/2)(eqQ)_{\text{atomic}}}$$

defined by Goldstein.⁹ This quantity is a measure of the number of electronic charges lost by the bromine in double bond formation. Assuming an $(eqQ)_{\text{atomic}}$ for Br⁷⁹ of 769.6 Mc/sec¹⁰ the value of δ becomes 0.12 indicating roughly a 12% contribution of structure III.

⁹ J. H. Goldstein, J. Chem. Phys. **24**, 106 (1956).

¹⁰ B. P. Dailey and C. H. Townes, J. Chem. Phys. **23**, 118 (1955).

The individual contributions of structures I and II may be estimated from χ_{zz} by using the method of Townes and Dailey¹¹ assuming a pure p covalent bond in structure I. The resulting contributions are 49% for struc-

¹¹ V. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

ture I and 39% for structure II. It should be emphasized that the above estimates of the percent contribution of each structure are very crude, and will undoubtedly require revision as more is learned concerning the relation of quadrupole coupling to chemical bonds.

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Distribution of Vibrational Frequencies of a Crystal by Fourier Transformation of the Heat Capacity

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It is shown that when represented on a logarithmic temperature scale a thermodynamic function is the *resultant* or convolution of the frequency distribution function and a function characteristic of a single oscillator. The inversion to yield the frequency distribution function may be accomplished by means of a theorem on the Fourier transform of a resultant. The method is related to that of Montroll, but may be in a more practical form for calculation. The present formulation also yields a quantitative expression for the error in the frequency distribution function which shows the importance of adequate smoothing of the experimental data.

INTRODUCTION

MONTROLL¹ has given a general method for the calculation of the frequency distribution of a crystal by inversion of the thermodynamic functions (energy, heat capacity, etc.). Although Montroll's derivation makes use of the theory of Fourier transforms, this is not evident from the form of his final formulas. The latter are expressed in terms of the Riemann zeta function of complex argument, which has apparently not been tabulated for a sufficient range for practical application of the formulas. Another variation of the Fourier transform method has been given by Kroll.² His method makes use of a procedure which has been widely used in the past in treating experimental data, namely, the representation of the heat capacity by computing at each temperature an effective Debye characteristic temperature. The now classic work of Born and von Kármán, Blackman, etc.,¹ as well as a recent and very important theoretical discussion by Van Hove,³ have shown that the frequency distribution for a periodic lattice departs radically from the Debye form for a continuum except at the lowest frequencies. Thus, the replacement of the heat capacity by the Debye characteristic temperature over the entire experimental temperature range seems somewhat anachronistic at present. (Of course, the Debye function may be used legitimately for extrapolation to 0°K.) The subsequent steps in Kroll's method also seem rather difficult, involving as they do the inversion of the characteristic temperature function, the evaluation of a

series of Bessel functions of complex arguments, and finally, two numerical integrations.

The present paper describes still another variation of the Fourier transform method which seems more practical at present than that of Montroll and more straightforward than that of Kroll. The writer arrived at this method independently of the work of Montroll and Kroll as a result of the observation that, when plotted on a logarithmic temperature scale, the heat capacity is the *resultant*⁴ of the frequency distribution function and a function characteristic of a single oscillator. The inversion follows immediately from a theorem on the Fourier transform of a resultant. The method requires the initial calculation of the Fourier transform of the harmonic oscillator function. The calculation of the frequency distribution then involves the Fourier transformation of the heat capacity, followed by a second Fourier transformation of the quotient of the preceding two transforms.

THEORY

It is convenient to represent each frequency, ν , by its characteristic temperature, $\theta = h\nu/k$, and to let $g(\theta)d\theta$ be the number of frequencies having θ in a given interval $d\theta$. The contribution of a single harmonic oscillator to the thermodynamic function, $f(T)$, will be denoted by $h(\theta/T)$. Then, as a result of the statistical independence of the oscillators,

$$f(T) = \int_0^\infty g(\theta)h(\theta/T)d\theta, \quad (1)$$

and it is required to calculate the frequency distribution

¹ E. W. Montroll, J. Chem. Phys. **10**, 218 (1942).

² W. Kroll, Prog. Theoret. Phys. (Japan) **8**, 457 (1952).

³ L. Van Hove, Phys. Rev. **89**, 1189 (1953). See also H. B. Rosenstock, Phys. Rev. **97**, 290 (1955).

⁴ E. C. Titchmarsh, *Theory of Fourier Integrals* (Oxford University Press, New York, 1948).