UNIVERSITY OF CINCINNATI

13 May 1933

I hereby recommend that the thesis prepared under my supervision by Roland Schaffert

entitled The Infrared Absorption Spectra and Molecular Structure of NO_2 and N_2O_4.

be accepted as fulfilling this part of the requirements for the degree of Ph. D

Approved by:

Louis T. More

Form 668—G. S. and Ed.—1M—7-31

THE INFRARED ABSORPTION SPECTRA

AND

MOLECULAR STRUCTURE OF

NO_2 AND N_2O_4

A dissertation submitted in partial
fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

to the Graduate School of the
University of Cincinnati

1933

by

ROLAND MICHAEL SCHAFFERT, A.B., Doane College,
1930; M.A., University of Cincinnati, 1931

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

Introduction

In 1904, Drude, from the study of the dispersion of various substances was led to the conclusion that the infrared absorption and emission bands of most substances (including gases) must be due to the vibrations of electrically charged atoms and molecules, rather than to the oscillations of electrons inside the atoms. In 1912 Bjerrum extended the conceptions of Drude, and with the accumulation of data, it soon became evident that much was to be learned about molecular dynamics and structure from a study of infrared absorption spectra.

The simplicity of the diatomic structure prompted extensive investigations on this type of molecule, both experimentally and theoretically. The experimental observations of a single fundamental frequency with a number of harmonics, and the appearance of double branches of fine structure in these bands led to a successful explanation of the dynamics of this molecule in the light of the quantum theory. Such a molecule could be represented by a mechanical dumb-bell model with an elastic bond.

An extension of these ideas to the polyatomic molecule has only begun, and complete analysis of the structure and dynamics of even the simplest kinds of polyatomic molecules has been reached in only a few cases.

The infrared absorption of nitrogen peroxide has been investigated by Daniels[1], and by Warburg and Leithauser[2] in the region 2μ to 7μ . They observed bands at approximately 3.4μ, 5.7μ and 6.12μ. Von Bahr[3] observed bands at 6.1μ and 7.3μ for this substance[4].

In order to obtain the fundamental frequencies and to attempt an analysis of the molecular structure of NO_2 and N_2O_4, it was decided to investigate the infrared absorption of nitrogen peroxide and extend the observations into the longer wavelength region.

Although a considerable amount of investigation on this equilibrium mixture has been carried out in the field of chemistry, very little is known at the present time concerning those properties which contribute to a knowledge of the structure of the molecules NO_2 and N_2O_4.

For an analysis of the structure of polyatomic molecules from the fundamental frequencies it is necessary to make certain assumptions regarding the binding forces between pairs of atoms. A mathematical treatment of the vibrational problem, even for the less complex polyatomic molecules, will

---

[1]Daniels, Jour. Amer. Chem. Soc., 47, p. 2856, 1925
[2]Warburg and Leithauser, Ann. d. Physik, 28, p. 313, 1909
[3]Eva von Bahr, Ann. d. Physik, 33, p. 585, 1910

[4]During the course of this investigation C. R. Bailey and A.B.D. Cassie have reported observstions on this gas to 18μ and report several additional bands. Nature, vol. 131, p. 239, 1933.

in general give a set of equations which are less in number than the unknown quantities contained in them. These unknowns are the force constants and the angles describing the geometrical arrangement of the atomic centers. If the molecule contains a number of like atoms, and if there is good evidence of several equal bonds, the symmetry of the configuration will, in some cases, reduce the unknowns so as to render solutions of the equations possible.

Hints regarding structure are in some cases obtained from a knowledge of the electric moment of the molecule[5], e. g., in the triatomic molecule the absence of a permanent electric moment is a good argument for a linear model, while an appreciable electric moment indicates a triangular structure. It has also been pointed out by Rawlins[5] that, if the specific heat of a triatomic molecule at low temperatures approaches that of a diatomic molecule, a linear, or nearly linear structure is to be expected. These considerations at the present time are not sufficient to determine uniquely the structure of polyatomic molecules, but are valuable as guides in choosing a molecular model consistent with infrared data.

Although the fundamental frequencies are in many cases obtained from the Raman spectra, it is necessary, especially in the case of gases, to resort to the infrared absorption

---

[5]Rawlins, Trans. of Faraday Soc., p. 927, Sept. 1929

spectra for a more complete analysis.

The spectrometer used in the present investigation did not permit resolution of any of the bands into rotational fine structure, and interpretation of the results is therefore confined to the vibrational aspect of the molecules.

Apparatus

A Leiss prism spectrometer of the Wadsworth type was used. The experimental arrangement is shown in Fig. 1. N is a Nernst glower; M_1, M_2, M_3, M_4, concave mirrors; m_1, m_3, plane mirrors, m_2, Wadsworth mirror; S_1, S_2, slits; P, rocksalt prism; T, thermopile; G_1, primary galvanometer and thermo-relay amplifier; G_2, secondary galvanometer; K_2, scale for reading deflections of G_2; R, extension for rotating prism table; L, telescope for reading angle of rotation on scale K_1; S, shutter; C_1, C_2, absorption cells; W, mica or rocksalt window.

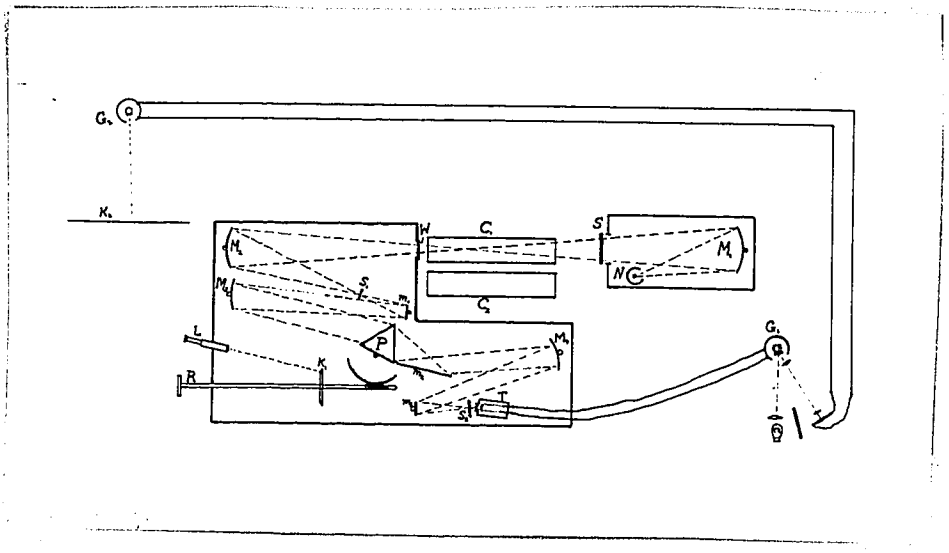


Fig. 1. Experimental arrangement.

The spectrometer was enclosed in a felt-lined box. The cells, shutter and spectrometer were arranged so that they could be operated by one observer. A Moll thermo-relay amplifier, used in connection with a Zernike galvanometer for primary deflections and a sensitive Leeds & Northrup galvanometer for secondary deflections, proved to be very useful in studying the longer wavelength regions where the emission of the glower was comparatively weak. A Moll linear thermopile, enclosed in an air-tight brass case and placed immediately behind the exit slit, was used to detect the radiation.

The spectrometer was adjusted according to the method suggested to the author by W. W. Sleator of the University of Michigan. The prism was first adjusted so that the entering beam of light striking the face of the prism is reflected back through the entrance slit so that the reflected image exactly fills the slit. The angle of incidence of the mercury green line (5461) was then computed from the minimum deviation formula and the known index of refraction of NaCl at this wavelength. The prism was then turned through this angle and the Wadsworth mirror adjusted so that the Hg green line filled the opening of the second slit. The spectrometer was then checked with the Hg emission line at 1.614μ and the CO_2 absorption band at 4.26μ. The indices of refraction for NaCl, taken from tables[6], were plotted on a

---

[6]Schaefer & Matossi, Das Ultrarote Spektrum, p. 47.

graph with wavelengths through a range .5μ to 16μ. On a separate graph the angle of minimum deviation was plotted with the indices of refraction . The wavelength for any angle of the prism table could then be determined by referring to the two graphs and correcting for the change in the indices of refraction due to the temperature of the prism.

The sensitivity of the receiving apparatus was sufficient to obtain readings as far as 16μ with the NaCl prism, although the transmission of rocksalt in this region is small.

Preparation of the Gas

Pure nitrogen peroxide was obtained by heating C. P. copper nitrate and condensing the gas by cooling with a mixture of ice and CaCl. The apparatus, shown in Fig. 2, was made entirely of pyrex glass. In chamber A, water present in the copper nitrate was condensed, the gas passing through a drier of P_2O_5 and being condensed at C. The gas was forced into the absorption cell by partially evacuating the cell. In this process it was again passed through P_2O_5 to insure dryness.

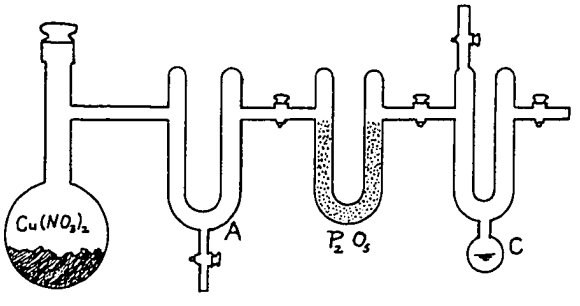


Fig. 2. Apparatus for preparing nitrogen peroxide.

Absorption Spectra of NO_2 and N_2O_4

The spectrum of nitrogen peroxide was mapped from 2μ to 16μ, using absorption cells 10 cm. in length with rock-salt windows and slit widths ranging from .08 mm. to .5 mm. Strong absorption bands were observed at 3.3μ, 5.7μ, 6.14μ, 7.28μ, 7.85μ, 13.3μ and 15.6μ, and a weak band at 3.89μ. These bands with their approximate intensities are shown in Fig. 3.

SEE NEXT PAGE

Fig. 3. Infrared absorption spectra of NO_2 and N_2O_4.

The observations on these bands were taken at a pressure of one atmosphere. The low intensity of the band at 3.89μ did not permit accurate measurement of its wavelength.

It is known from chemistry that at ordinary tempera-

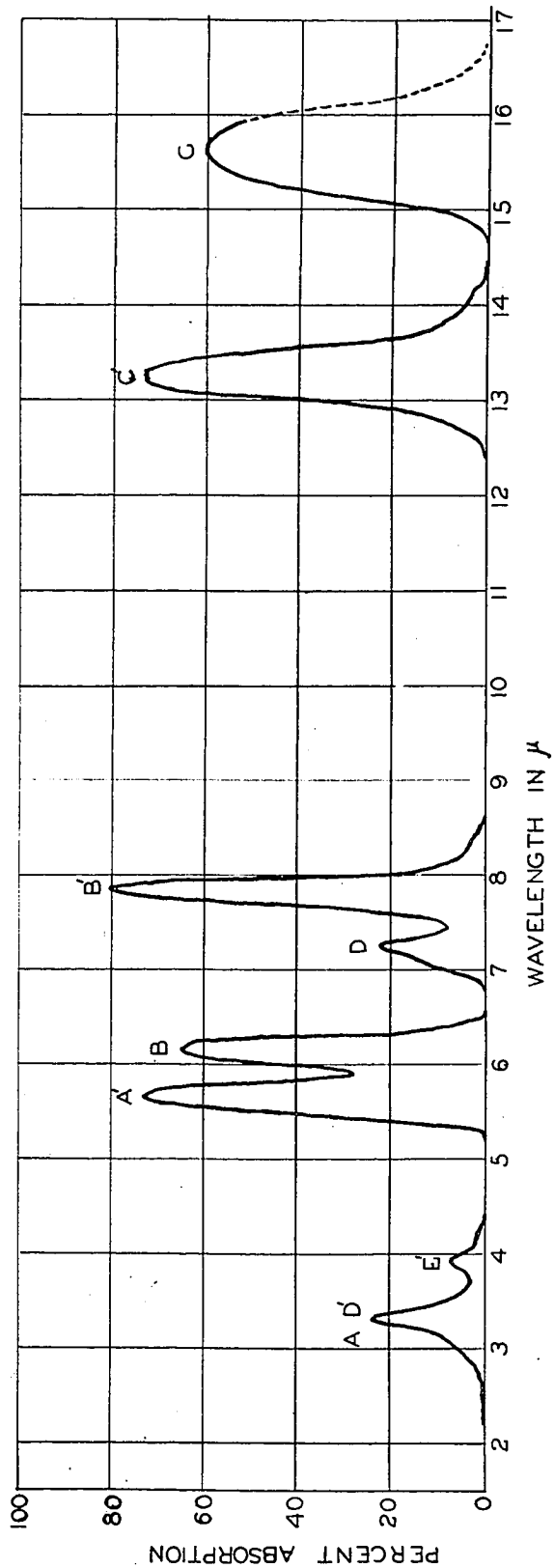


Fig. 3. The infrared absorption spectra of NO_2 and N_2O_4.

tures this gas is a mixture of NO_2 and N_2O_4. At about 150° C, however, the gas consists entirely of NO_2.

In order to determine which bands were due to NO_2 and which were due to N_2O_4, an investigation of the infrared absorption of this gas was undertaken at different temperatures. The gas was heated by using an absorption cell with nichrome wire wound about its outer surface and insulated from the surface with asbestos. The temperature was regulated by the amount of current passed through the nichrome coil, and observed by inserting a thermometer in a side tube attached to the absorption cell.

For the region, 2μ to 8μ, mica windows were used with cells 35 cm. in length. The results for this region are shown in Figs. 4 and 5. The bands at 3.89μ, 5.7μ and 7.85μ are due to N_2O_4, since they decrease in intensity and finally disappear at the higher temperatures and increase in intensity at the lower temperatures. The bands at 6.14μ and 7.28μ increase in intensity as the temperature is raised and decrease when the temperature is lowered, and are therefore attributed to NO_2. The band at 3.3μ exhibits a peculiarity inasmuch as it decreases slightly with increase in temperature and increases in intensity with decrease in temperature, but does not disappear at the higher temperatures as we would expect if it were due only to N_2O_4. This suggests that the 3.3μ band may be a characteristic fre-

quency of NO_2 and N_2O_4, and that the absorption bands of both gases in this region are nearly superimposed.

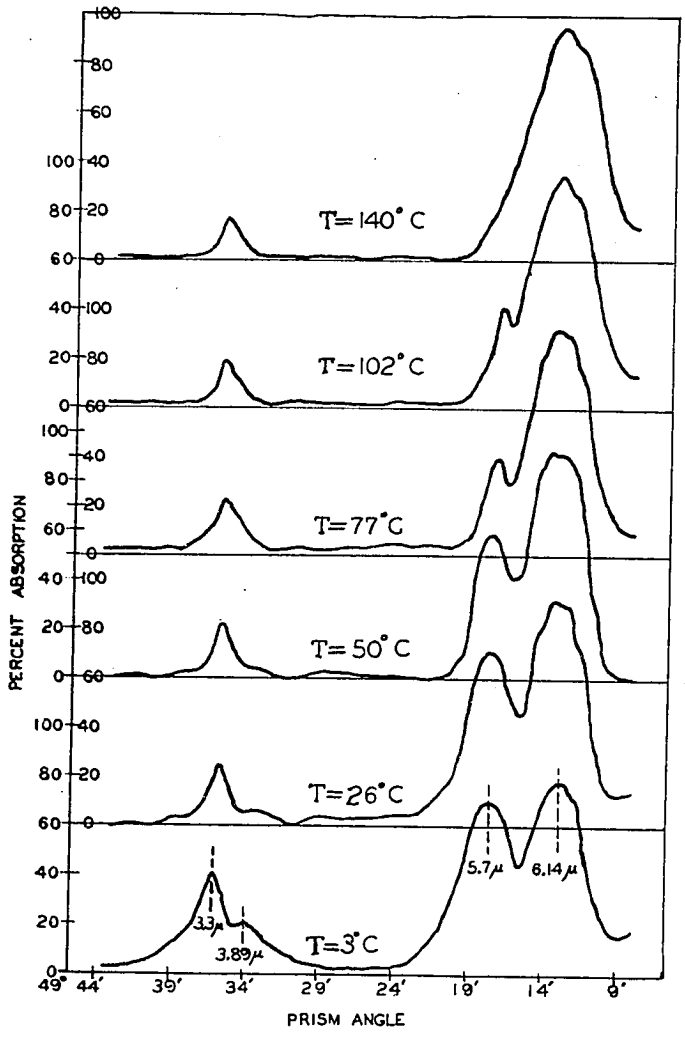


Fig. 4. Infrared absorption of nitrogen peroxide at different temperatures in the region 2μ to 7μ.

For the region , 8μ to 16μ it was necessary to use rocksalt windows on the absorption cells. To avoid breaking of the rocksalt windows, the cells were first fitted

with mica windows. Openings were then cut in the mica and the rocksalt windows mounted over these openings with duco cement . This reduced the strain on the rocksalt and prevented cracking when the cell was heated.

Observations in this region were taken at temperatures of 25° C and 150° C. The band at 13.3μ disappeared entirely

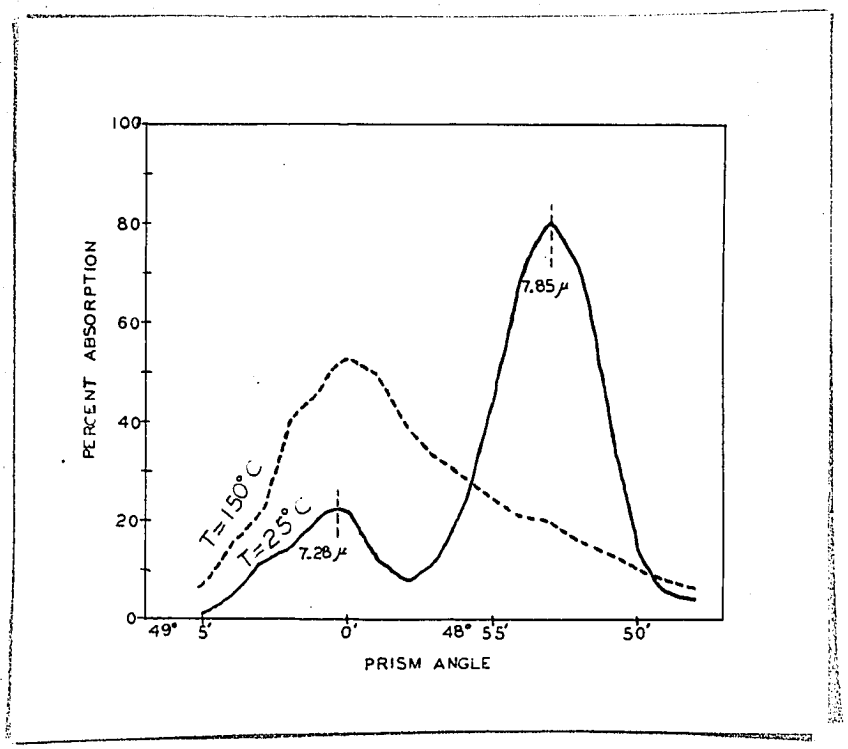


Fig. 5. Infrared absorption of nitrogen peroxide at different temperatures in the region 7μ to 8μ.

at 150° C while 15.6μ band remained at about the same intensity.

These experiments were sufficient to determine with

some degree of certainty which bands could be attributed to the two different types of molecules present in this gas mixture. The bands designated as A, B, C, and D in Fig. 3. are due to NO_2 while the bands A', B', C', E' and possibly a band near 3.3μ (D') are due to N_2O_4.

It may be remarked here that Bailey and Cassie[4] report the disappearance of all the bands except bands B and C at a temperature of 100° C, and apparently did not observe the band at 7.28μ. The author has examined the 3.3μ and 7.28μ bands at temperatures as high as 240° C with some care. Both bands remained at these high temperatures, the 7.28μ band increasing considerably in intensity.

The low transmissibility of NaCl in the region of 16μ did not permit complete observation of the band at 15.6μ. Bailey and Cassie give the wavelength of this band as 15.6μ, and in the following calculations their value has been adopted.

Infrared Absorption of Liquid Nitrogen Peroxide

In order to determine whether or not the 3.3μ band was common to both NO_2 and N_2O_4, it was decided to investigate the infrared absorption of liquid N_2O_4. Since this liquid boils at about 21° C, it was necessary to construct an absorption cell which could be cooled well below this temperature. The difficulties encountered in obtaining a

suitable cell for this liquid were many, and a number of cells were tried and discarded. The details of the cell finally used are shown in Fig. 6. Two sheets of mica 7 inches long, 1.5 inches in width and 0.1 mm. in thickness were separated by a mica "gasket" 0.1 mm. in thickness and clamped between two slotted brass strips. The top was left open so that a small pointed tube could be inserted between the mica plates. The upper portion of the cell was surrounded by a cooling chamber. The cell was filled with liquid N_2O_4 by forcing gaseous nitrogen peroxide into the cell through the small pointed tube inserted at the top, and condensed by cooling. Ater the cell had been filled the top was closed by clamping the mica sheets together with the brass insert B, and sealed over with soft wax. The

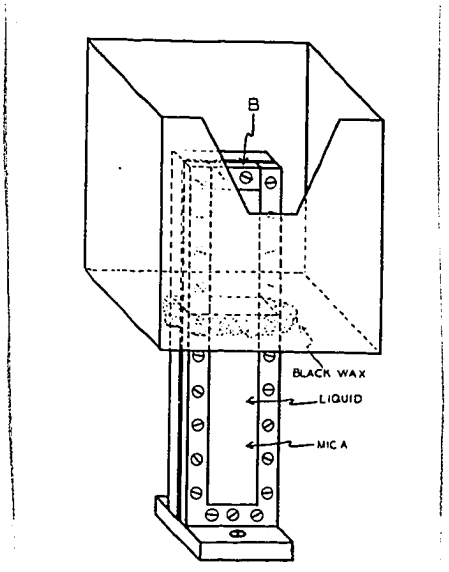


Fig. 6. Cell used in studying liquid N_2O_4.

cell was then placed in the light path so that the beam passed through the lower portion. An empty cell of the same thickness of mica was attached so that both cells could be thrown alternately in and out of the path of light.

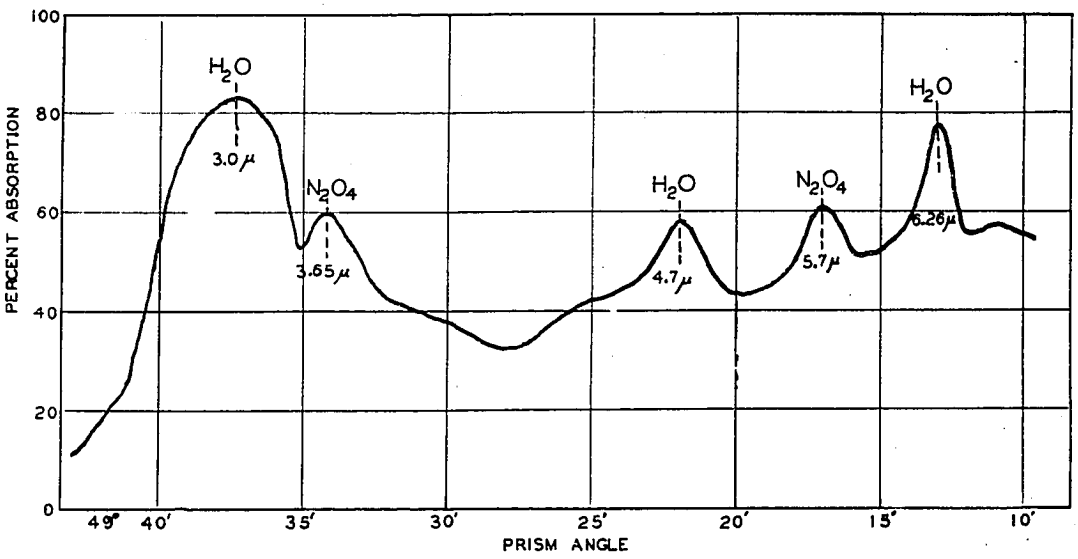


Fig. 7. Infrared absorption of liquid N_2O_4.

The results were not very gratifying and were made less certain due to the condensation of water vapor on the windows of the absorption cell. However, in addition to the H_2O bands at 3μ, 4.7μ and 6.26μ, bands due to N_2O_4 were observed at 3.65μ and 5.7μ, as shown in Fig. 7. The nearness of the broad H_2O band at 3μ made the wavelength

measurements of the 3.65μ band uncertain, and it is probable that its true wavelength is somewhat less than this value.

Discussion of Bands

These results show that N_2O_4, at least in the liquid state does have an absorption band in the region of the 3.3μ band of NO_2. The fact that the peak of the 3.3μ band shows no appreciable shift at the higher temperatures suggests that the N_2O_4 band in this region has approximately the same frequency as the NO_2 band in the gaseous state. It is interesting also to note that this summation frequency, $\nu_1 + \nu_3$, for N_2O_4 has almost the same value as the frequency, ν_3, for NO_2 as shown in Table I. The observed value for this frequency is 3008 cm^{-1}.

The frequencies and wavelengths of the absorption bands for NO_2 and N_2O_4 are shown in Table I. In the following discussion the bands will be referred to by the symbols A, B, C, etc. ν_1, ν_2, and ν_3 are the fundamental frequencies which were found to be consistent with calculations, and ν_3 refers to the unsymmetrical frequency.

Table I

NO_2:

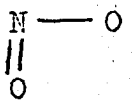
Band	Observed frequency in cm^{-1}.	Calculated frequency in cm^{-1}.	Combination	Wavelength in μ
A	3008		ν_3	3.36
B	1628		ν_2	6.14
C	641		ν_1	15.60
D	1373	1380	$\nu_3 - \nu_2$	7.28

N_2O_4:

Band	Observed frequency in cm^{-1}.	Calculated frequency in cm^{-1}.	Combination	Wavelength in μ
A'	1754		ν_3	5.70
B'	1274		ν_1	7.85
C'	752		ν_2	13.30
D'	3008	3028	$\nu_1 + \nu_3$	3.30
E'	2570	2500 or 2526	$\nu_2 + \nu_3$ or $2\nu_1$	3.89

Structure of NO_2

The nature of the chemical binding in NO_2 has not been definitely decided. Mecke[7] however, gives good evidence from thermochemical considerations that this molecule has a double bond between one of the O-atoms and the N-atom and a single bond connecting the other O-atom to the N-atom, or symbolically



Binding of this type would indicate an unsymmetrical structure. Bailey and Cassie[4] attribute only the bands B and C to NO_2 and conclude that the molecule is linear and symmetrical with an inactive fundamental at about 11μ. Consideration of the existence of the three active fundamentals, A, B and C, with and active combination band D, in the light of Dennison's[8] discussion regarding the conditions for the existence of such bands, would indicate that the NO_2 molecule is not a symmetrical linear structure.

So far as the author is aware no data are available concerning the electric momemt of this molecule. Strong and Woo[9] have studied the far infrared absorption of nit-

---

[7]Mecke, Z. f. Phys. Chem., B, 7, p. 114, 1930.
[8]Dennison, Rev. of Modern Phys., 3, pp. 289-298, 1931.
[9]Strong and Woo, Phys. Rev., 42, p. 275, 1932.

rogen peroxide by the reststrahlen method, but did not find any appreciable absorption bands in this region. The amount of dissociation of this gas at room temperature, however, is only about 20 per cent.

The normal modes of vibration of the atoms in an unsymmetrical triatomic molecule have been evaluated by Lechner[10] using the "valence force" system, and by Radakovic[11] for the "central force" system.

Lechner's equations for the normal frequencies are as follows:

$$
\begin{aligned}
& n_1^2 + n_2^2 + n_3^2 = k_{12}/\mu_{12} + k_{23}/\mu_{23} + d/\mu_4 \\
& n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2 = \frac{k_{12}k_{23}}{\mu_{12}\mu_{23}}\left(1 - \frac{\mu_{12}\mu_{23}}{m_2^2}\cos^2\alpha\right) + \\
& \qquad + \frac{k_{12}d}{\mu_{12}\mu_4}\left(1 - \frac{\mu_{12}\mu_4}{m_2^2}\frac{s^2}{s_{23}^2}\cdot\sin^2\alpha\right) + \\
& \qquad + \frac{k_{23}d}{\mu_{23}\mu_4}\left(1 - \frac{\mu_{23}\mu_4}{m_2^2}\frac{s^2}{s_{12}^2}\cdot\sin^2\alpha\right) \qquad (1) \\
& n_1^2 n_2^2 n_3^2 = \frac{k_{12}k_{23}}{\mu_{12}\mu_{23}}\frac{d}{\mu_4}\left(1 - \frac{\mu_{12}\mu_{23}}{m_2^2}\right) .
\end{aligned}
$$

Where, $n = 2\pi\nu c$; α is the supplement of the valence angle; k_{12} and k_{23} are the force constants for the normal modes along the lines joining the masses m_1 to m_2 and m_2 to m_3;

---

[10] Lechner, Akad. d. Wiss., Wien, Sitzungsber., 141, p. 291, 1932.

[11] Radakovic, Monatsh. f. Chem., 56, p. 447, 1930.

d is the effective deformation constant; s_{12} and s_{23} are the distances between m_1 and m_2 and m_2 and m_3 respectively; s is related to s_{12} and s_{23} by the equation,

$$d_{12}s_{12}^2 = d_{23}s_{23}^2 = d\,s^2$$

and

$$\frac{1}{\mu_{12}} = \frac{1}{m_1} + \frac{1}{m_2}, \qquad \frac{1}{\mu_{23}} = \frac{1}{m_2} + \frac{1}{m_3}$$

$$\frac{1}{\mu_4} = \frac{1}{\mu_{12}}\cdot\frac{s^2}{s_{12}^2} + \frac{2}{m_2}\cdot\frac{s^2}{s_{12}s_{23}}\cdot\cos\alpha + \frac{1}{\mu_{23}}\frac{s^2}{s_{23}^2}$$

For NO_2 these become

$$\frac{1}{\mu_{12}} = \frac{1}{\mu_{23}} = \frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}, \qquad m_1 = m_3 = m, \quad m_2 = M,$$

$$\frac{1}{\mu_4} = \frac{s^2}{\mu}\left(\frac{1}{s_{12}^2} + \frac{1}{s_{23}^2}\right) + \frac{2}{M}\frac{s^2}{s_{12}s_{23}}\cos\alpha \qquad \text{----------(2)}$$

where, m = mass of O-atom

M = mass of N-atom.

If we accept Mecke's conclusion that one double and one single bond are present in the NO_2 molecule, and assume that the force constant for the double bond is twice that of the single bond[12], we can write,

---

[12] Dadieu and Kohlrausch, Ber. d. Deutch. Chem. Gesell., 63, p. 276, 1930, have found this to be approximately true for the bonds in a number of molecules.

$$k_{12} = 2\ k_{23} = 2\ k\ .$$

Then, if we let,

$$\frac{k}{\mu} = x\ , \quad \frac{d}{\mu_4} = z\ ,$$

$$A = n_1^2 + n_2^2 + n_3^2$$

$$B = n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2$$

$$C = \frac{n_1^2 n_2^2 n_3^2}{(1 - \mu^2/M^2)}$$

and

$$D = \frac{\mu \mu_4}{M^2} s^2 \sin^2 \alpha \left(\frac{2}{s_{23}^2} + \frac{1}{s_{12}^2} \right) \qquad \text{----------(3)}$$

equations (1) become,

$$3\ x + z = A \qquad \text{----------(4)}$$

$$2\ x^2 \left(1 - \frac{\mu^2}{M^2} \cos^2 \alpha \right) + x\ z\ (3 - D) = B \qquad \text{--------(5)}$$

$$2\ x^2 z = C \qquad \text{----------(6)}$$

Eliminating z from (4) and (6), we get

$$6\ x^3 - 2\ A\ x^2 + C = 0 \qquad \text{----------(7)}$$

From (5),

$$D = 3 + \frac{2\ x^2 \left(1 - \frac{\mu^2}{M^2} \cos^2 \alpha \right) - B}{x\ z} \qquad \text{----------(8)}$$

Eliminating $\mu_4 s^2$ from (2) and (3), we get

$$(D M^2 - 2\mu^2\sin^2\alpha)\, v^2 + 2 D M\mu\cos\alpha \cdot v + (D M^2 - \mu^2\sin^2\alpha) = 0 \qquad \text{----------(9)}$$

which is a quadratic in v, where

$$v = \frac{s_{12}}{s_{23}} .$$

Now, if we take as fundamental frequencies for NO_2, the values,

$\nu_1 = 641\ cm^{-1}$

$\nu_2 = 1628\ cm^{-1}$

$\nu_3 = 3008\ cm^{-1}$

x and z can be evaluated from equations (4) and (7).

Equation (7) gives three values for x. For NO_2 only one of these gave real values for v, namely;

$$x = 3.0140 \times 10^{28} .$$

Using this value of x, the positive values of v, as obtained from (9), were plotted with the values of α. The curve is shown in Fig. 8. If we restrict the values of v, so that $v < 1$, the range of possible values for the angle α lie between 78° 30' and 128°. This restriction is allowable, since the distance s_{12} for the double bond would be expected to be less than s_{23} for the single bond.

Furthermore, if we take

$$s = \frac{s_{12} + s_{23}}{2}$$

and substitute, $d/\mu_4 = z$ in equation (2), we get

$$d = \frac{\pm z\mu M v^2}{(M + 2\mu v \cos \alpha + M v^2)} \frac{1}{(v + 1)^2} \qquad \text{----------(10)}$$

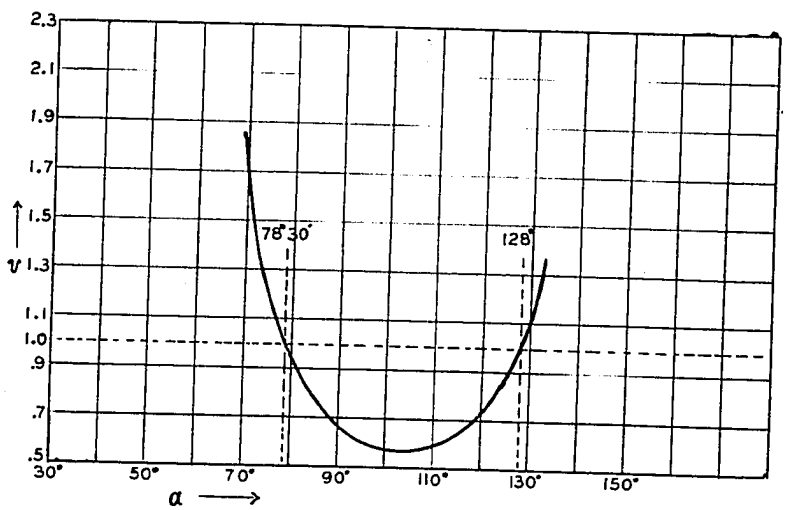


Fig. 8. Curve showing v as a function of α.

The curve describing d as a function of α, obtained by substituting values of v from the curve in Fig. 8, in equation (10), is shown in Fig. 9. This curve shows a maximum at 82° and a minimum at 95° in the range of permissible values of α.

Since one of the modes of vibration gives rise to a periodic change of the angle α about an equilibrium posi-

tion, the maximum and minimum values can be taken as the two possible equilibrium positions for α. At these points

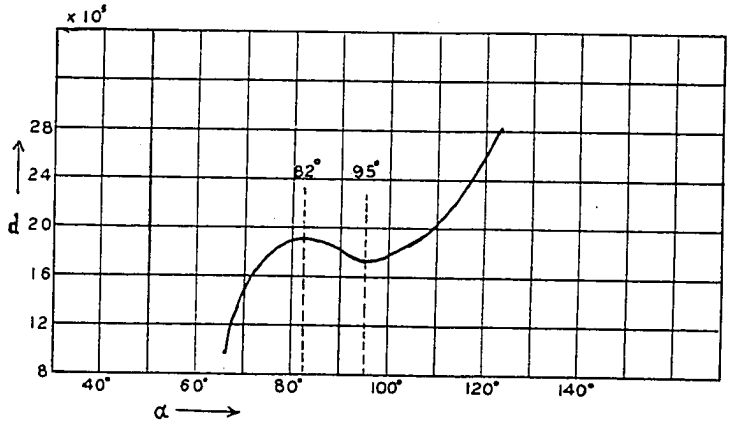


Fig. 9. Curve showing d as a function of α.

d remains approximately constant for small changes of α. Of these two positions, the value α = 95°, at which position d is a minimum, would give the most stable configuration for the molecule.

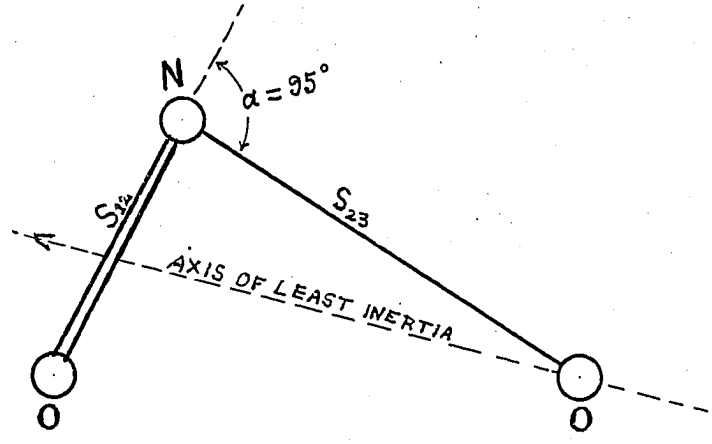


Fig. 10. Structure of NO_2 molecule.

From this point of view the structure of the NO_2 molecule in the unexcited state would be that of an unsymmetrical triangle with the valence angle $(180^\circ - \alpha)$ equal to 85°, Fig. 10.

The Molecular Constants

The doublet separation of band B was found to be approximately 33 cm . Bailey and Cassie[4] give the doublet separation for this band and band C as 35 cm and 32 cm respectively. This frequency difference corresponds to a moment of inertia of 4.2×10^{-39} g. cm^2. If this is identified with the moment about the axis of least inertia, the interatomic distances s and s are 1.9 Å and 3.2 Å respectively, and if this value of the moment of inertia is taken as the moment about the greatest axis of inertia these distances become 0.69 Å and 1.17 Å. The former appear to be the more likely values.

The axis of least inertia for this unsymmetrical structure was found to be along a line in the plane of the molecule, passing through the center of gravity and the center of the O-atom of greatest distance from the N-atom.

The equations giving the normal frequencies for this unsymmetrical molecule are not sufficient to determine which of these is the so-called unsymmetrical frequency. If we can apply to this unsymmetrical structure the con-

clusions of Dennison[14] and Bailey and Cassie[15] regarding the orientation of the electric doublets effective in the vibrations of symmetrical triatomic molecules, it would appear that the bands B and C are the symmetrical frequencies for NO_2. The doublet separations of both bands are approximately equal which indicates a probable similarity of structure.

The four observed frequencies can be represented by such an expression as $(n_1\nu_1' + n_2\nu_2' + n_3\nu_3')$, where ν_1' and ν_2' are the symmetrical frequencies and ν_3' the unsymmetrical frequency. For bands B and C, $n_3 = 0$, and the effective electric doublet is perpendicular to the axis of least inertia; for bands A and D, $n_3 = 1$, and the electric doublet is parallel to this axis. This would indicate the presence of a Q-branch in the bands A and D, while the bands B and C would have only P- and R-branches. The structure of these bands is uncertain due to the low resolving power of the spectrometer used.

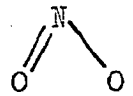
A summary of the molecular characteristics, as calculated for the NO_2 molecule, are given in Table II. The force

---

[14]Dennison, Rev. Mod. Phys., 3, p. 280, 1931.
[15]Bailey and Cassie, Proc. Royal Soc., 130, p. 142, 1930; 137, p. 622, 1932.

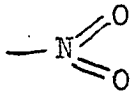
constants were calculated from equation (10) and the relations, $x = k/\mu$, $k = k_{23}$, $k_{22} = 2k$.

Table II

MOLECULE	Fundamental frequencies in cm^{-1}	Force constants dynes/10^{-5}	Atomic distances cm x 10^{-8}	Valence angle $(180-\alpha)$	Moment of Inertia
NO_2 	= 1628	$k_{22} = 7.38$	$s_{22} = 1.9$	85°	$I = 4.2 \times 10^{-39}$ g. cm
	= 641	$k_{23} = 3.69$	$s_{23} = 3.2$		
	= 3008	d = 17.4			

Structure of N_2O_4

The simplicity of the spectrum of N_2O_4 makes it appear probable that this molecule consists of two symmetrical nitro-groups with a linkage between the N-atoms. The frequencies characteristic of each group will then be alike, and if the binding,



is adopted for each of the nitro-groups, these two groups may be represented by isosceles triangular forms.

The equations for the normal frequencies of an isosceles triangular model, as taken from Lechner's paper[16], are as follows:

$$n_3^2 = \frac{k}{m}\left\{\frac{m}{M}(1 + \cos\alpha) + 1\right\}$$

$$n_1^2 n_2^2 = \frac{k}{m}\cdot\frac{2d}{m}\cdot\frac{2m + M}{M} \qquad (1)$$

$$n_1^2 + n_2^2 = \frac{k}{m}\left\{\frac{m}{M}(1 - \cos\alpha) + 1\right\} + \left(\right.$$

$$+ \frac{2d}{m}\left\{\frac{m}{M}(1 + \cos\alpha) + 1\right\}$$

where the symbols have the same meaning as in the preceding discussion.

Eliminating k and d from these equations, we get

$$\frac{n_1^2 n_2^2}{n_3^2}\cdot\frac{M}{2m + M}\cdot u^3 - (n_1^2 + n_2^2 + n_3^2)\,u + 2n_3^2\left(\frac{m}{M} + 1\right) = 0 \quad ---(2)$$

where,

$$u = \frac{m}{M}(1 + \cos\alpha) + 1 ,$$

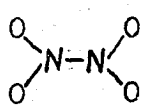
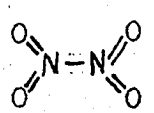
and n_3 refers to the unsymmetrical frequency.

---

[16] Bjerrum, Verh. Deutche Phys. Gesell., vol. 16, p. 737, 1914, and Yates, Phys. Rev., 36, p. 555, 1930, also give theoretical treatments of this model.

Substitution in (2) of the values for the fundamental frequencies (A', B', and C', Table I) gives two solutions for the angle α; one when ν_3' is taken as 1274 cm^{-1} and one when $\nu_3' = 1754$ cm^{-1}. These, together with the corresponding force constants, are shown in Table IV.

Table IV

Molecule	Unsymm. frequency in cm^{-1}	Symm. frequencies in cm^{-1}	Force constants dynes/10^{-5}	Valence angle $(180° - \alpha)$
	Case I $\nu_3' = 1274$	$\nu_1' = 1754$ $\nu_2 = 752$	k = 4.9 d = 2.58	139° 20'
	Case II $\nu_3' = 1754$	$\nu_1' = 1274$ $\nu_2 = 752$	k = 9.7 d = 0.6	135° 20'
Nitro-compounds $R \cdot NO_2$	$\nu_3' = 1560$	$\nu_1' = 1380$	k = 9.48	103°
Organic nitrates $R \cdot O \cdot NO_2$	$\nu_3' = 1627$	$\nu_1' = 1274$	k = 9.33	116° 40'

These values are compared with those given by Dadieu and Kohlrausch[17] for the NO_2-groups in nitrocompounds and

[17] Dadieu and Kohlrausch, Monatsh. f. Chem., 58, p. 437, 1931.

organic nitrates, calculated from the Raman frequencies for these substances.

Case II, with $\nu_3' = 1754$ cm and $k = 9.7 \times 10^5$ is in good agreement with the values for the force constants given by Dadieu and Kohlrausch, and appears to be consistent with the double bond structure of the NO_2-groups.

Deformation of the N_2O_4 Molecule in Solution

Daniels[1] has investigated the infrared absorption of NO_2 and N_2O_4 in solution, in the region 2μ to 7μ, and made the interesting observation that the N_2O_4 band, originally at 5.7μ in the gaseous state, was shifted toward the shorter wavelengths in solution. He used eight different solvents and found that the 5.7μ band was shifted to wavelengths varying from 5.45μ to 5.3μ. The NO_2 bands at 3.3μ and 6.14μ remained unchanged in position.

In Case II of the preceding discussion this 5.7μ band was selected as the unsymmetrical frequency in the NO_2-groups. With chloroform as a solvent Daniels observed that this frequency had shifted to $\nu_3' = 1852$ cm. If this value is substituted in the equation,

$$n_3^2 = \frac{k}{m}\left\{\frac{m}{M}\left(1 + \cos\alpha\right) + 1\right\}$$

where, $k = 9.7 \times 10^5$

the value of α turns out to be approximately equal to zero, or the valence angle is approximately equal to 180°.

This means that the two nitro-groups in N_2O_4 have been changed from the isosceles triangular form in the gaseous state, to a linear structure in solution. NO_2 in solution apparently maintains its original structure. This is consistent with the values obtained for the deformation constants in NO_2 and N_2O_4. For NO_2, $d = 17.4 \times 10^5$, while for N_2O_4, $d = 0.6 \times 10^5$. This large difference would render the N_2O_4 molecule much more susceptible to angular deformation.

Summary

(1) The infrared absorption spectrum of nitrogen peroxide has been investigated in the gaseous and liquid states, using a prism spectrometer. Absorption bands were observed at 3.3μ, 3.89μ, 5.7μ, 6.14μ, 7.28μ, 7.85μ, 13.3μ, and 15.6μ in the gaseous state, and at 3.65μ, and 5.7μ in the liquid state.

(2) By heating the gas to a temperature of 150° C, it was found that the bands at 3.89μ, 5.7μ, 7.85μ and 13.3μ were due to N_2O_4, while those at 3.3μ, 6.14μ, 7.28μ and 15.6μ were due to NO_2.

(3) The problem of the normal vibrations of the NO_2 and N_2O_4 has been discussed from the standpoint of the "valence force" system.

(4) The structure of the NO_2 molecule agrees with that of an unsymmetrical triangular form with unequal bonds between the N-atom and the respective O-atoms, while the N_2O_4 molecule can be best represented by two symmetrical nitro-groups with a linkage between the N-atoms.

(5) The deformation of N_2O_4 in solution was calculated, and it was found that the nitro-groups change from an isosceles triangular form to a linear structure.

The author wishes to express his thanks to his advisor, Dr. L. T. More, and to other members of the staff of the Physics Department for suggestions and help during the course of this investigation.