Electron Diffraction by the Oxides of Nitrogen

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Electron Diffraction by the Oxides of Nitrogen

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Electron diffraction has been obtained by the transmission of electrons (20–35 kv) through molecular beams of N_2O, NO_2, N_2O_4 and N_2O_5. The molecular structure determinations were made by using the complete electron scattering formula including the incoherent scattering. The results can be summarized as follows: (1) *Nitrous oxide;* for a linear model the separation of the end atoms was found to be 2.38 ± 0.05A in exact agreement with Wierl's measurement on this structure. Unfortunately it is impracticable to distinguish between models of the form $N-O-N$ and $N-N-O$. (2) *Nitrogen dioxide;* no diffraction rings were observed which is to be expected if the molecule is triangular with the $N-O$ distance 1.15 to 1.3A. (3) *Nitrogen tetroxide;* the presence of one diffraction ring at $(1/\lambda) \sin \theta/2 = 0.455 \pm 0.01$ lead to the conclusion that the $N-N$ distance is 1.6 to 1.7A for the model O_2N-NO_2. No definite angular relationship between the two planes containing the NO_2 groups could be determined. (4) *Nitrogen pentoxide;* again only one diffraction ring was observed. It occurred at a slightly greater angle than for N_2O_4 giving $(1/\lambda) \sin \theta/2 = 0.474 \pm 0.004$. The symmetrical model $O_2N-O-NO_2$ with the $N-O$ distance 1.3 to 1.4A gave a calculated interference pattern in best agreement with this result.

THE diffraction of electrons by gases has been used as a method for determining the structure of molecules.[1] This analysis involves the interference theory originally developed for coherent x-ray scattering with the inclusion of the atomic electron scattering amplitudes. The importance of the incoherent electron scattering has been determined theoretically by Morse[2] and later summarized by Bewilogua.[3] For the purpose of obtaining nuclear separations it is usually unnecessary to consider the incoherent scattering; however, in some instances it should be included. These considerations will be discussed in the present work and a treatment of the structure determinations of the nitrogen oxides will be undertaken.

The angular distribution of coherent electron scattering can be expressed in the following manner:[4]

$$I(x) \sim \sum_{i=1}^{n} \sum_{j=1}^{n} \psi_i \psi_j (\sin x_{ij})/x_{ij},$$

where $I(x)$ is the intensity of scattering at angle θ per unit intensity of the primary beam at unit distance from the scattering molecule, while $x_{ij} = 4\pi l_{ij}(\sin \theta/2)/\lambda$. Recent workers[5] have simplified this expression to the extent of replacing the scattering amplitude $\psi_i = Z_i - F_i/(\sin \theta/2)^2$ by simply Z_i (atomic number), an approximation although justifiable in some cases cannot be generally applied as will be shown below. A more complete electron scattering formula can be written as follows:[6]

$$I(x) = \frac{k}{((\sin \theta/2)/\lambda)^4} \times$$
$$\left[\sum_{i=1}^{n} \sum_{j=1}^{n} (Z_i - F_i)(Z_j - F_j) \frac{\sin x_{ij}}{x_{ij}} + \sum_{i=1}^{n} Z_i S(\nu_i) \right]$$

where $\nu_i = 4\pi b_i(\sin \theta/2)/\lambda$ while b_i is expressed in Angstroms and represents the characteristic

[1] R. Wierl, Ann. d. Physik **8**, 521 (1931); **13**, 453 (1932); Hengstenberg and Brú, Anales, Soc. Espana. Fis. y Quim. **30**, 341 (1932); **31**, 115 (1933); L. O. Brockway and Linus Pauling, Proc. Nat. Acad. Sci. **19**, pp. 68 and 860 (1933); L. O. Brockway, ibid. **19**, 303 (1933); **19**, 868 (1933); S. B. Hendricks, Louis R. Maxwell, V. M. Mosley and M. E. Jefferson, J. Chem. Phys. **1**, 549 (1933); Ralph W. Dornte, J. Chem. Phys. **1**, 566 and 630 (1933); J. Am. Chem. Soc. **55**, 4126 (1933); H. Braune and S. Knoke, Zeits. f. physik. Chemie **B21**, 297 (1933).

[2] Ph. M. Morse, Phys. Zeits. **33**, 443 (1932).

[3] L. Bewilogua, Phys. Zeits. **33**, 688 (1932).

[4] Cf., J. Chem. Phys. **1**, 549 (1933).

[5] R. Wierl, Ann. d. Physik **13**, 453 (1932); L. O. Brockway and Linus Pauling, reference 1; Ralph W. Dornte, J. Am. Chem. Soc. **55**, 4126 (1933).

[6] L. Bewilogua, reference 3; also see Phys. Zeits. **32**, 740 (1931).
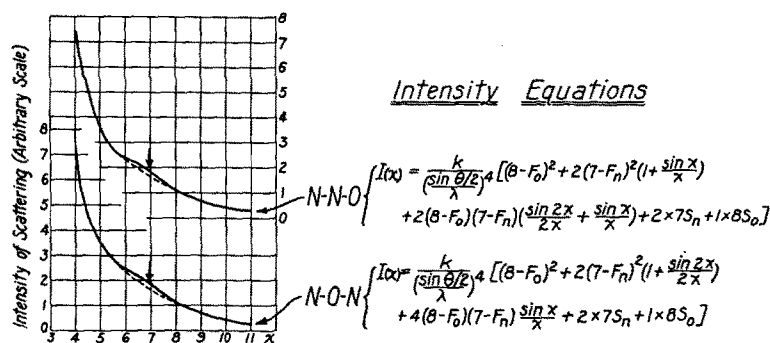
MAXWELL, MOSLEY AND DEMING

FIG. 1. Theoretical electron scattering curves for N_2O where $x=4\pi(1.1A)$ $(\sin \theta/2)/\lambda$.

atomic length for incoherent scattering and is given by $b_i = 0.176/Z_i^{\frac{1}{3}}$. $S(\nu_i)$ is a function of the parameter ν_i which has the value 0 for $\nu_i = 0$ but converges to unity for large values of ν_i. k is a constant. The second term in the above equation expresses the amount of incoherent scattering.

The experimental apparatus used has already been described,[7] in which 20–35 kv cathode rays were projected through the beam of molecules under consideration. Scattering produced at small angles was recorded on a photographic plate located 26.2 cm from the scattering region and the diameter of the diffraction rings were measured by means of a recording microphotometer.

NITROUS OXIDE

Wierl[8] has obtained electron scattering from N_2O and found a diffraction ring occurring at $(1/\lambda) \sin \theta/2 = 0.468$ giving an $N-N$ distance of $2.38\pm0.06A$ for a model of the form $N-O-N$. This result has been confirmed in the present work in which case a value of $(1/\lambda) \sin \theta/2 = 0.465\pm0.01$ was obtained. Unfortunately it is very difficult to distinguish between the two possible linear forms of the molecule as illustrated in Fig. 1. The calculations are represented by the curves for the two cases and the formulas used are also shown. F_i, the atomic scattering factors were obtained from the calculated values of James and Brindley.[9] The two curves are practically indistinguishable and therefore make

differentiation between the two forms very difficult. This is caused by the fact that the nitrogen and oxygen atoms scatter in nearly the same manner so that interchanging them does not alter materially the intensity curves. Likewise for the molecular models to be considered below, although reasonable allocations have been given to the nitrogen atoms, the electron diffraction methods cannot exclude the possibility of other arrangements for the nitrogen atoms with the same interatomic distances.

Additional information on the structure of N_2O has been determined from other sources as follows: *Band Spectra*. From an investigation of the infrared spectrum of N_2O Snow[10] concluded that the molecule is linear and has the symmetrical form $N-O-N$. Later Plyler and Barker[11] extended the range of wave-lengths to include a number of bands not previously obtained. From the properties of the spectrum they found that the model $N-N-O$ agreed more precisely with the observation than either the $N-O-N$ structure or the triangular model. Badger on calculating the moment of inertia from Plyler and Barker's data arrived at the value of 66.7×10^{-40} g cm^2 which has been used by Pauling[12] to give a structure resonating between the Lewis structures :$\ddot{N}$::N::$\ddot{O}$: and :N:::N:$\ddot{O}$: where the $N-N$ and $N-O$ distances are 1.10 and 1.22A, respectively, consistent with the electron diffraction results. (2) *Electric Moment.* There is some disagreement among various

[7] S. B. Hendricks, Louis R. Maxwell, V. M. Mosley and M. E. Jefferson, J. Chem. Phys. 1, 549 (1933).
[8] R. Wierl, reference 1.
[9] R. W. James and G. W. Brindley, Phil. Mag. 12, 81 (1931).
[10] C. P. Snow, Proc. Roy. Soc. A128, 294 (1930).
[11] E. K. Plyler and E. F. Barker, Phys. Rev. 38, 1827 (1931).
[12] Linus Pauling, Proc. Nat. Acad. Sci. 18, 293, 498 (1932).

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workers on the value of the permanent electric moment of N_2O. Braunmühl[13] obtained a value of 0.25×10^{-18} while later Ghosh, Mahanti and Mukherjee[14] as well as Schwingel and Williams[15] concluded that the electric moment is zero. However, recently Watson, Rao and Ramaswamy[16] find that the moment is not zero but has the small value of 0.17×10^{-18}. On the basis of a finite electric moment the model $N-N-O$ appears to be most probable.

NITROGEN DIOXIDE

In the case of scattering from NO_2 it was necessary to shift the equilibrium, $2NO_2 \leftrightarrows N_2O_4$ toward high concentrations of NO_2. This was accomplished by streaming the vapor through a heating bath at approximately 175°C and then to the diffraction apparatus where the walls and tip of the molecular jet were maintained at about 150°C. Under these conditions the scattering observed was produced by NO_2 and photographs were taken with voltages ranging from 27 to 36 kv. From thirteen exposures there were obtained no visible diffraction rings within the range of $(1/\lambda) \sin \theta/2$ from 0 to 0.6. Microphotometer records made on three typical plates also showed no evidence of rings.

Fig. 2 shows the results of the calculations made for the determination of the structure of this molecule. As in the previous case the incoherent scattering has been included. From the set of curves obtained it is seen that curves Nos. 4 and 9 show no maxima while No. 3 exhibits only a faint prominence. The experimental results are not sufficient to distinguish among these three curves so that the photographs are in agreement with any of the following forms:

$$N-O = 1.15A, \quad \alpha = 120°$$
$$N-O = 1.15A, \quad \alpha = 90°$$
$$N-O = 1.30A, \quad \alpha = 90°$$

[13] V. Braunmühl, Phys. Zeits. **28**, 141 (1927).

[14] P. N. Ghosh, P. C. Mahanti and B. C. Mukherjee, Zeits. f. Physik **58**, 200 (1929).

[15] C. H. Schwingel and J. W. Williams, Phys. Rev. **35**, 855 (1933).

[16] For a more complete discussion of the electric moment of N_2O see H. E. Watson, G. G. Rao and K. L. Ramaswamy, Proc. Roy. Soc. **A143**, 558 (1934).
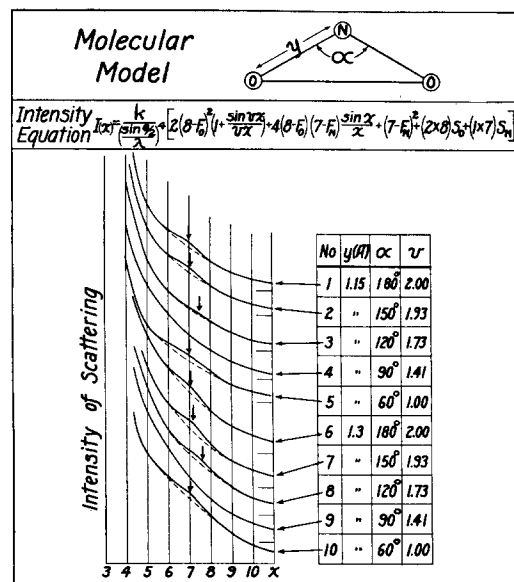

FIG. 2. Theoretical electron scattering curves for various models of NO_2 where $x = 4\pi y (\sin \theta/2)/\lambda$.
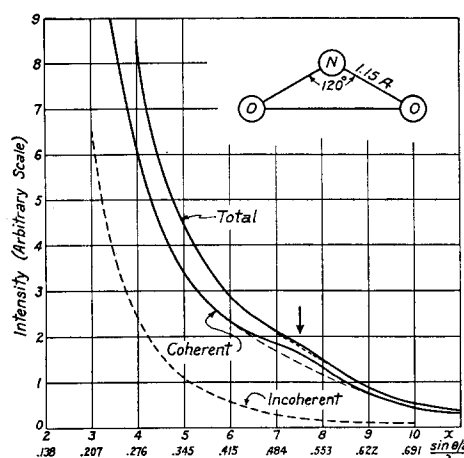

FIG. 3. Theoretical electron scattering curves for NO_2 illustrating an instance where the prominence of the diffraction ring is considerably decreased by the introduction of the incoherent scattering. Similar curves for benzene have been computed by Bewilogua.[3]

which are considered to be the most likely structures of the molecule.

An example of the effectiveness of the incoherent scattering in reducing the prominence of the diffraction ring as computed by only the coherent scattering is illustrated in Fig. 3. Thus the use of incoherent scattering causes the model $N-O = 1.15A$, $\alpha = 120°$ to come within the possible structures consistent with the experiments that otherwise would have been excluded.

TABLE I. *Comparison of various methods used for determining the theoretical position of electron diffraction rings.*

Molecule	Position of Diffraction Ring (x)			Error introduced by approx. sol.
NO_2	Coherent scattering[1]	Approximate solution[2]	Complete solution[3]	
$\alpha = 90°$, $N-O = 1.15A$	6.0 (weak)	7.6	none	—
$\alpha = 120°$, $N-O = 1.15A$	7.5	8.0	7.5 (very weak)	6.7%
$\alpha = 150°$, $N-O = 1.15A$	7.1	7.5	7.1	5.6%
$\alpha = 90°$, $N-O = 1.30A$	none	7.6	none	—
$\alpha = 120°$, $N-O = 1.30A$	7.5	8.0	7.58	5.5%
$\alpha = 150°$, $N-O = 1.30A$	7.1	7.5	7.2	4.2%

[1] ψ_i expressed completely.
[2] Coherent scattering with ψ_i replaced by Z_i, incoherent scattering omitted.
[3] Both coherent and incoherent scattering included with ψ_i expressed completely.

Table I shows a comparison of the different methods used for computing the diameter of the diffraction rings. The error introduced by the simplified treatment varies from 4 to 6 percent for the cases considered here and is not sufficiently exact to indicate those models which will produce no interference maxima. Considerable information is thereby lost by such treatment since the absence of diffraction rings may be equally important for structure determinations.

From a consideration of the values of the dielectric constant and index of refraction of NO_2 Ghosh and Mahanti[17] have predicted that the molecule is not linear and that the electric moment should be 0.62×10^{-18}, while recently Zahn[18] has found the electric moment to be 0.3×10^{-18} agreeing with a triangular model.

From studies of the infrared absorption spectra Bailey and Cassie[19] suggested that the molecule is linear with an $N-O$ distance of 1.1A, a model which is definitely excluded by the electron diffraction results. Whereas Harris, Benedict and King[20] who examined the absorption bands of NO_2 under high resolution conclude that the molecule is not arranged in a linear form.

NITROGEN TETROXIDE

In order to obtain electron diffraction from N_2O_4 the heating bath and molecular jet were permitted to cool down to room temperature. The source of liquid N_2O_4 in the boiler was maintained at approximately its boiling point 21.5°C or atmospheric pressure, in which case there exists a mixture of 75 percent N_2O_4 and 25 percent NO_2. However, this pressure was reduced before the gas reached the molecular jet and was further reduced at the region in the diffraction chamber where the scattering occurred. Under these conditions a diffraction ring was obtained which is illustrated by the microphotometer record shown in Fig. 4.

Fourteen photographs were taken for wavelengths varying from 0.066A to 0.073A and the average value of $(1/\lambda) \sin \theta/2$ was found to be 0.455 ± 0.01. A complete set of calculated scattering curves are shown in Fig. 5, together with the position of the experimental diffraction ring for comparison. Since these computations were made for pure N_2O_4 a direct comparison is not justifiable until the amount and effect of NO_2 present is determined. The concentration of NO_2 can be obtained from an estimate of the pressure in the diffraction region. Lenard[21] has found a

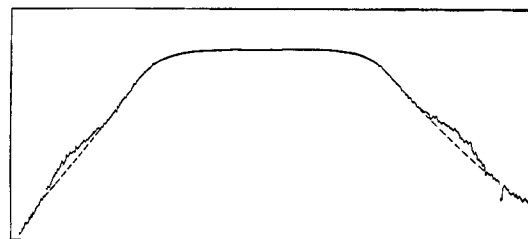[17] P. N. Ghosh and P. C. Mahanti, Phys. Zeits. **30**, 531 (1929).
[18] C. T. Zahn, Phys. Zeits. **34**, 461 (1933).
[19] C. R. Bailey and A. B. D. Cassie, Nature **131**, 239 (1933).
[20] Louis Harris, W. S. Benedict and G. W. King, Nature **131**, 621 (1933).

FIG. 4. Densitometer record for N_2O_4.

[21] P. Lenard, Ann. d. Physik **12**, 714 (1903).

TABLE II. *Theoretical electron diffraction maxima from N_2O_4, NO_2 mixtures.*

Model No. of N_2O_4	Position of Maximum (x)			
	100% N_2O_4	50% N_2O_4, 50% NO_2	25% N_2O_4, 75% NO_2	10% N_2O_4, 90% NO_2
1	7.5	7.5	7.45	7.5
2	8.1	8.0	8.05	none
3	6.8	7.0	7.05	"
6	7.4	7.3	7.2	7.6 (weak)
7	6.4	6.45	none	none
8	7.0	7.0	6.9	"
9	6.5	6.8	7.0 (weak)	"
10	6.0	6.1	none	"

Experimental position 6.58 ± 0.16; Model No. 3 used for NO_2.

value of 0.005 cm^{-1} per mm Hg for the specific absorption coefficient of air for 30 kv electrons. Assuming that air has approximately the same absorption as $N_2O_4 \rightleftarrows 2NO_2$, it is then possible to estimate the pressure of the diffraction region. The diameter of the opening in the molecular jet was 0.4 mm with the beam diverging in a manner approximating the cosine distribution law. The electron beam clears the opening of the jet by less than $\frac{1}{2}$ mm so that the depth of the beam at the point of scattering can be taken to be about 2 mm. If one further assumes that the primary beam intensity is decreased by 10 percent in order to yield a diffraction pattern then the pressure in the diffraction region using Lenard's

data should be 0.14 atmosphere, in which case there would be not less than 50 percent dissociation in the region of diffraction. If the pressure were reduced to as low as 0.01 atmospheres the gas would be 90 percent dissociated. The effect on the position of the N_2O_4 diffraction ring by the addition of NO_2 is exemplified in Table II. The model chosen for NO_2 was the $N-O=1.15A$, $\alpha=120°$. Decreasing the percentage of N_2O_4 results chiefly in the reduction in size of the prominences rather than changing materially their positions. Even for the extreme case of 10 percent N_2O_4 many of the maxima have been entirely lost; however those which are still retained have not been appreciably displaced.

From a consideration of these computations we arrive at the following possible structures of N_2O_4:

$N-N=1.6A$,	$\beta=0°$	$N-O=1.15A$,	$\alpha=120°$
$N-N=1.7A$,	$45°<\beta<90°$,	$N-O=1.15A$,	$\alpha=120°$
$N-N=1.6A$,	$\beta=0°$	$N-O=1.15A$,	$\alpha=90°$.

This is equivalent to specifying that the $N-N$ distance is 1.6 to 1.7A without definitely fixing the angular relationship between the two NO_2 groups.

Sutherland[22] has measured the infrared absorption spectrum and Raman scattering of N_2O_4 and found that the molecular form O_2N-NO_2 was definitely more probable than the other radically different structures such as $O-N-O$ $-NO_2$ and $O-N-O-O-N-O$. The first form is preferred on account of the ease of dissociation into NO_2 and satisfactorily explains the outstanding features of the infrared and Raman
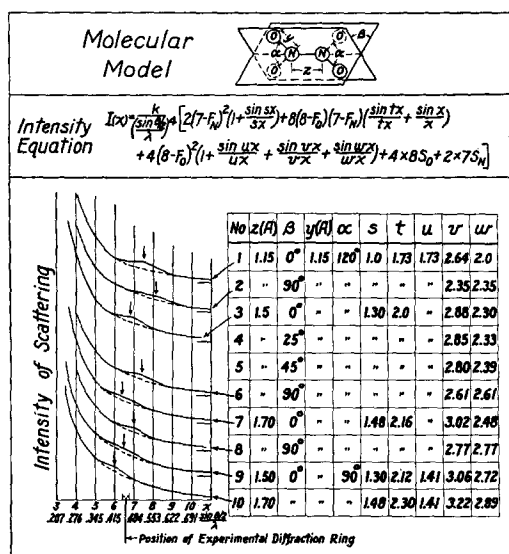

FIG. 5. Theoretical electron scattering curves for various models of N_2O_4 where $x=4\pi y (\sin\theta/2)/\lambda$. A comparison with the position of the experimental diffraction maxima should be made after consulting Table II which shows the effect of the presence of NO_2.

[22] G. B. B. M. Sutherland, Proc. Roy. Soc. A141, 342, 535 (1933).

scattering. Also evidence was obtained against location of the NO_2 groups at right angles to each other, i.e., $\beta = 90°$. Harris and King[23] have recently concluded from the infrared absorption spectra that the NO_2 groups may not lie in the same plane and that they are joined together by the nitrogen atoms.

From x-ray diffraction photographs of solid N_2O_4 Vegard[24] has proposed that the crystal lattice is built up of linear and symmetrical NO_2 groups. Hendricks[25] has interpreted Vegard's results as signifying that the solid is made of O_2N-NO_2 groups with $\alpha = 120°$, β from 0 to 25° and the $N-N$ distance within the range of 1.1 to 1.7A.

Nitrogen Pentoxide

N_2O_5[26] gave an interference pattern quite similar to N_2O_4, with a single diffraction ring occurring at a slightly greater angle, giving $(1/\lambda) \sin \theta/2 = 0.474 \pm 0.004$. The temperature of the substance was raised to between 25° and 40°C which afforded sufficient vapor pressure to obtain diffraction. However, the substance was maintained at these temperatures for less than 10 minutes which was time enough to obtain a set of photographs. This prevented the formation of any undesirable amount of products of decomposition. Fig. 6 shows a typical densitometer record of N_2O_5 while the theoretical scattering curves are given in Fig. 7. Molecular models Nos. 2 and 8 give the best agreement with the experiment although the position of the experimental maxima is definitely smaller than the theoretical value expressed in terms of the
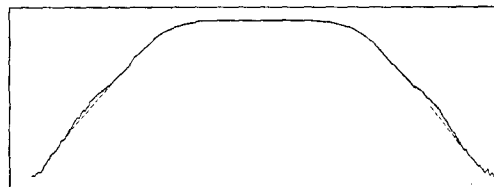
[23] Louis Harris and G. W. King, J. Chem. Phys. **2**, 51 (1934).

[24] L. Vegard, Zeits. f. Physik **68**, 184 (1931); **71**, 299 (1931).

[25] Sterling B. Hendricks, Zeits. f. Physik **70**,699 (1931).

[26] N_2O_5 was prepared by treating $N_2O_4 \leftrightarrows 2NO_2$ with ozone, after the method of Demetric Helbig, R. Accad. dei Lincei, Atti Scienze, (5a) S12, 211 (1903).
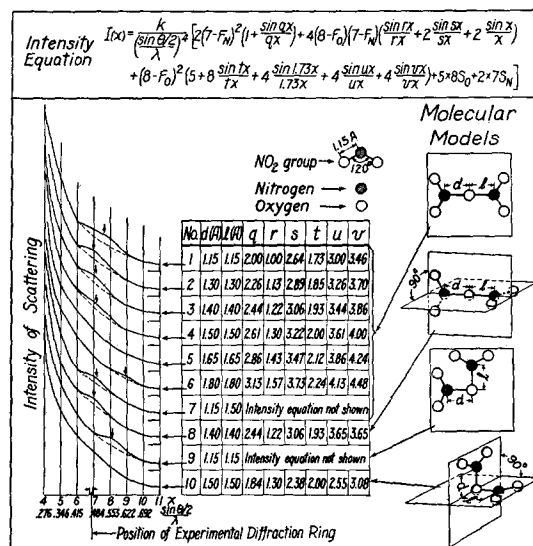
Fig. 6. Densitometer record for N_2O_5.

Fig. 7. Theoretical electron scattering curves for various models of N_2O_5 where $x = 4\pi(1.15A)$ $(\sin \theta/2)/\lambda$.

variable $x = 4\pi y(\sin \theta/2)/\lambda$. y was taken to be 1.15A, one of the possible distances for the NO_2 group as previously determined. If we now substitute in this equation $x = 7$ (theoretical value), and $(\sin \theta/2)/\lambda = 0.474$ (experimental value) we obtain $y = 1.18A$. Since this distance is only slightly different from the assumed value, the position of the diffraction ring would not be appreciably altered by this change in the $N-O$ distance of the NO_2 group. Thus we can arrive at a model in good agreement with the experimental result, namely $N-O = 1.3$ to 1.4A with $y = 1.18A$.