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THE INFRARED ABSORPTION SPECTRA OF
NITROGEN DIOXIDE

by

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A Thesis Submitted in Partial Fulfilment of
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October 12, 1950.

Dr. L. W. Dunlap,
Librarian,
University of British Columbia.

Dear Dr. Dunlap:

This letter will certify that the thesis of Mr. W. L. Ross has been carefully studied by the undersigned, and that the thesis meets the required standards and an abstract has been approved by the Department.

Yours sincerely,

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GMS:lc

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ABSTRACT

An automatic calibration marker and wave-length scanning drive has been installed on the Perkin-Elmer infrared spectrometer and the precision of this drive was checked under various operating conditions. The optimum reproducibility was found to be 0.03 wave-drive divisions, and the reproducibility under normal operating conditions was found to be 0.23 wave-drive divisions at the slowest scanning speed, which is six minutes per revolution of the wave-drive drum.

The spectrum of nitrogen dioxide has been examined in the NaCl and LiF prism regions, and a tentative assignment of the absorption bands has been made.

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An automatic calibration marker and wavelength scanning drive has been installed on the Perkin-Elmer infrared spectrometer and the precision of this drive was checked under various operating conditions. The optimum reproducibility was found to be 0.03 wave-drive divisions and the reproducibility under normal operating conditions was found to be 0.23 wave-drive divisions at the slowest scanning speed, which is six minutes per revolution of the wave-drive drum.

The spectrum of nitrogen dioxide has been examined in the NaCl and LiF prism regions and a tentative assignment of the absorption bands has been made.

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THE INFRARED ABSORPTION SPECTRUM OF
NITROGEN DIOXIDE

I

INTRODUCTION

1. The Present State of the Information regarding the Nitrogen Dioxide Molecule.

The infrared spectrum of NO_2 has been investigated by Sutherland (20), Schaffert (18), Penny (21) and others. At present the following assignment of absorption bands appears to be most satisfactory (13).

$$\nu_2 = 648 \text{ cm}^{-1}$$

$$\nu_1 = 1320 \text{ cm}^{-1}$$

$$\nu_3 = 1621 \text{ cm}^{-1}$$

This assignment of the infrared spectrum leads to the conclusion that NO_2 is a non-linear symmetrical molecule which has an ONO bond angle of 120° . The force constants are:

$$f_{\text{No}} = 9.13 \times 10^5 \text{ dynes/cm.}$$

$$f_{\text{Oo}} = 4.34 \times 10^5 \text{ dynes/cm.}$$

Harris and King (5) have obtained a value of 154° for the ONO bond angle from ultraviolet absorption measurements. On the other hand, electron diffraction measurements have shown that the ONO bond angle should be $130^\circ \pm 2^\circ$ and the NO bond distance should be 1.20 \AA (14). These values agree more closely with the values pre-

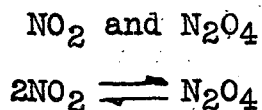
dicted by Pauling (17).

2. Object of the Research undertaken in this Thesis.

In this work an effort has been made to obtain the best precision possible in wavelength measurements from the Perkin-Elmer Infrared Spectrometer.

An attempt has also been made to recheck the previous work done on NO_2 to see if a reassignment of the infrared spectrum could be made which would be more in agreement with the structure predicted by other methods of investigation.

In order to study the spectrum of NO_2 , the fact that NO_2 is actually a mixture of NO_2 and N_2O_4 must be taken into account. This equilibrium reaction between



is shifted in favour of the formation of NO_2 at higher temperatures. For example, at 20°C the mixture is nearly all N_2O_4 whereas at 140°C only NO_2 exists. Therefore by examining the spectrum of the NO_2 and N_2O_4 mixture at different temperatures, it is possible to sort out the spectra of the two compounds.

II

THEORY

1. The concept of the normal vibrations of a molecule.

(a) The classical theory of normal vibrations

From a classical point of view, if a molecule contains N atoms which are vibrating with respect to each other in such a manner that an oscillating electric dipole exist, then electromagnetic radiation will be absorbed. The first problem to consider, is the determination of the nature of the vibrations that are possible in the molecule.

If an approximate model of the molecule is considered to be a system of N particles, in which the displacement from the equilibrium position of the i th particle is x_i y_i z_i and in which each particle is in a harmonic potential field, then if all but one particle remain in their equilibrium positions, the restoring forces on the displaced particle will be:

$$\begin{aligned} F_x^i &= -k_{xx}^{ii} x_i - k_{xy}^{ii} y_i - k_{xz}^{ii} z_i \\ F_y^i &= -k_{yx}^{ii} x_i - k_{yy}^{ii} y_i - k_{yz}^{ii} z_i \\ F_z^i &= -k_{zx}^{ii} x_i - k_{zy}^{ii} y_i - k_{zz}^{ii} z_i \end{aligned} \quad (1)$$

If none of the particles are constrained to their equilibrium positions, the forces on the i th particle will be:

$$\begin{aligned}
 F_x^i = & -k_{xx}^{i1} x_1 - k_{xy}^{i1} y_1 - k_{xz}^{i1} z_1 - \dots \\
 & \dots - k_{xx}^{ii} x_i - k_{xy}^{ii} y_i - k_{xz}^{ii} z_i - \dots \\
 & \dots - k_{xx}^{iN} x_N - k_{xy}^{iN} y_N - k_{xz}^{iN} z_N
 \end{aligned}
 \tag{2}$$

This expression is correct only if the restoring force for every displacement is 'harmonic'. However, if the displacements are small this can be a satisfactory approximation.

Now if all the particles, except one, remain in their equilibrium positions, this particle can execute simple harmonic motion as indicated in equation 3.

$$x_i = x_i^0 \sin(2\pi \nu t + \theta) \tag{3}$$

The restoring force will be;

$$F_x^i = m_i \ddot{x}_i = -4\pi^2 \nu^2 m_i x_i \tag{4}$$

However if the other particles do not remain in their equilibrium positions, there is a possibility that all the particles will vibrate with the same frequency according to simple harmonic motion. If this is so, then equation 4 must be satisfied for all particles simultaneously, that is:

$$\begin{aligned}
 -4\pi^2 N^2 m_i x_i &= -k_{xx}^{i'} x_i - k_{xy}^{i'} y_i - k_{xz}^{i'} z_i - \dots \\
 &\dots - k_{xx}^{i''} x_i - k_{xy}^{i''} y_i - k_{xz}^{i''} z_i - \dots \quad (5) \\
 &\dots - k_{xx}^{iN} x_i - k_{xy}^{iN} y_i - k_{xz}^{iN} z_i
 \end{aligned}$$

where $i = 1, 2, \dots, N$

These equations may be solved for the ratios of the displacements x_i, y_i, z_i if the determinant of the coefficients is zero. Since the force constants are fixed, then only specific values of the frequency will satisfy the following condition.

$$\begin{vmatrix}
 k_{xx}^{i'} - 4\pi^2 N^2 m_i & k_{xy}^{i'} & k_{xz}^{i'} & \dots & k_{xz}^{iN} \\
 k_{yx}^{i'} & k_{yy}^{i'} - 4\pi^2 N^2 m_i & k_{yz}^{i'} & \dots & k_{yz}^{iN} \\
 k_{zx}^{i'} & k_{zy}^{i'} & k_{zz}^{i'} - 4\pi^2 N^2 m_i & \dots & k_{zz}^{iN} \\
 k_{xx}^{2'} & k_{xy}^{2'} & k_{xz}^{2'} & \dots & k_{xz}^{2N} \\
 \dots & \dots & \dots & \dots & \dots \\
 k_{zx}^{N'} & k_{zy}^{N'} & k_{zz}^{N'} & \dots & k_{zz}^{NN} - 4\pi^2 N^2 m_N
 \end{vmatrix} = 0 \quad (6)$$

This determinant will have $3N$ roots. Of these, $3N-6$ will be different from zero ($3N-5$ if the system of particles is linear) and these represent the frequencies of the normal modes of vibration of the molecule. In general, any mode of vibration may be resolved into a linear combination of these normal vibrations. The remaining six zero frequencies are associated with displacements which have no restoring force, that is,

translations and rotations of the centre of mass of the system.

(b) Definition of Normal Coordinates

$$\text{if} \quad \begin{matrix} (1) & (1) & (1) \\ x_i & y_i & z_i \\ (2) & (2) & (2) \\ x_i & y_i & z_i \\ & & i = 1, 2, \dots, N \\ (3N) & (3N) & (3N) \\ x_i & y_i & z_i \end{matrix}$$

represent the displacements coordinates at any moment corresponding to the first, second, ----, $3N$ th normal mode of vibration, then it may be shown that for any normal mode, for example the j th mode of vibration, the ratio of the displacement coordinates $x_i^{(j)} : y_i^{(j)} : z_i^{(j)}$ $i = 1, 2, \dots, N$ is a constant.

That is

$$x_i^{(j)} : y_i^{(j)} : z_i^{(j)} = \xi_j (x_i^0 : y_i^0 : z_i^0) \quad \begin{matrix} i = 1, 2, \dots, N \\ j = 1, 2, \dots, 3N \end{matrix} \quad (7)$$

where

$$\xi_j = \xi_0 \sin(2\pi\nu_j t + \theta_j) \quad (8)$$

Thus the $\xi_1, \xi_2, \dots, \xi_{3N}$ which are called the normal coordinates, may be used to describe the vibration of the system of N particles.

(c) Quantum Mechanical treatment of Normal vibrations

The classical theory suffers from the objection that even though there are only $3N-6$ fundamental or normal modes of vibration, there are actually an infinite number of possible modes of vibration. An examination of the infrared spectrum of compounds indicates that this theory is not quite correct, since only $3N-6$ fundamental frequencies are found. Furthermore, this theory fails to explain the reasons for the occurrence of combination frequencies.

These objections are overcome to a considerable extent by a quantum mechanical treatment. The Schrodinger equation for a system of N particles is:

$$-\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \Delta_i \psi + V \psi = E \psi \quad (9)$$

This can be solved easily by separation of:

$$V = \sum_{i=1}^{3N} u_i(x_i) \quad (10)$$

where u_i is a function of only the i th position coordinate. This is true if the assumption that the classical vibrations in the molecule are strictly harmonic. It is still a satisfactory approximation if the vibrations are not strictly harmonic, but instead their amplitude is small.

It can be shown from equation 4 that:

$$V_x^i = \frac{1}{2} k_x x_i^2 \quad (11)$$

where V_x^i is the potential energy change for a change of the x coordinate from the equilibrium position to the i th particle. The total potential energy V is therefore:

$$V = \frac{1}{2} \sum \left(k_{xx}^{ij} x_i x_j + k_{yy}^{ij} y_i y_j + k_{zz}^{ij} z_i z_j \right) + \frac{1}{2} \sum \left(k_{xy}^{ij} x_i y_j + k_{yz}^{ij} y_i z_j + k_{zx}^{ij} z_i x_j \right) \quad (12)$$

By renaming the coordinates as follows:

$$x_i, y_i, z_i \ (i=1, 2, \dots, N) \longrightarrow q_1, q_2, \dots, q_{3N}$$

the expression for the potential energy becomes:

$$V = \frac{1}{2} \sum_{i,j}^{3N} k_{ij} q_i q_j \quad (13)$$

Similarly, the kinetic energy T

$$T = \frac{1}{2} \sum_i^N m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \quad \text{becomes} \quad T = \frac{1}{2} \sum_{i,j}^{3N} b_{ij} \dot{q}_i \dot{q}_j \quad b_{ij} = m_i \delta_{ij} \quad (14)$$

after the introduction of the new notation.

This may be simplified by the introduction of the concept of normal coordinates. It can be shown that (7)

$$V = \frac{1}{2} \sum_{i=1}^{3N} \lambda_i \xi_i^2 \quad \lambda_i = 4\pi^2 \nu_i^2 \quad (15)$$

$$T = \frac{1}{2} \sum_{i=1}^{3N} \xi_i^2 \quad (16)$$

Therefore the Schrodinger equation 9 becomes:

$$-\frac{\hbar^2}{2} \sum_{i=1}^{3N} \left(\frac{d^2}{d\xi_i^2} + \lambda_i \xi_i^2 \right) \psi = E \psi \quad (17)$$

by setting

$$\psi = \prod_{i=1}^{3N} \phi_i \quad (18)$$

the equation may be separated into

$$\sum_{i=1}^{3N} \left\{ \frac{1}{\phi_i} \frac{d^2 \phi_i}{d\xi_i^2} + \frac{2}{\hbar^2} \left(E_i - \frac{1}{2} \lambda_i \xi_i^2 \right) \right\} = 0 \quad (19)$$

where

$$E = \sum_{i=1}^{3N} E_i \quad (20)$$

These $3N$ equations have eigenfunctions

$$\phi_i(\xi_i) = N_{\nu_i} e^{-\frac{\lambda_i}{2} \xi_i^2} H_{\nu_i}(\sqrt{\lambda_i} \xi_i) \quad (21)$$

where the H_{ν_i} are the Hermite polynomials, and corresponding to these eigenfunctions there are the energy eigenvalues.

$$E_i = \hbar \nu_i \left(\nu_i + \frac{1}{2} \right) \quad (22)$$

where ν_i is the classical frequency of the i th mode of oscillation.

Thus the frequency of the observed spectrum lines should be given by the condition

$$\nu = \frac{E_i'' - E_i'}{h} \quad \text{or} \quad \bar{\nu} = \frac{E_i'' - E_i'}{c h} \quad (23)$$

Therefore 3N-6 fundamental absorption lines ($n_i, 0 \rightarrow 1$) should be expected. It is apparent that these frequencies directly related to the classical vibration frequencies of the molecule.

2. The Normal Vibrations of Nitrogen Dioxide

Since the force constants of any molecule are not always known, some other method of calculating the normal vibrations must be found. This calculation is most easily performed by considering the symmetry properties of the molecule. In order to do this, the following concepts must be introduced.

(a) Symmetry operations

These are operations such as rotations, reflections or inversions which transform the molecular model into an indistinguishable form. These operations are only possible when such symmetry properties are inherent in the molecule.

(b) Point Groups

Since certain symmetries or combinations of symmetry enforce other properties of symmetry on the molecular model, thus combinations of certain symmetry operations result in another symmetry operation on the same model. It may be shown (6), (3), that these combinations form closed groups according to the postulates of group theory.

(c) Effect of Symmetry Operations on eigenfunctions and Normal coordinates

If S is a symmetry operation which operates on the Schrodinger equation

$$H \psi_i = E_i \psi_i$$

(24)

The result is:

$$S H \psi_i = S E_i \psi_i$$

(25)

Since S only interchanges the particles, it can have no effect on the Hamiltonian operator H , furthermore, it will commute with the constant eigenvalue E_i , therefore:

$$H S \psi_i = E_i S \psi_i$$

(26)

If ψ_i is a non-degenerate eigenfunction, then only ψ_i or constant multiples of ψ_i will satisfy equation 25, therefore:

$$S \psi_i = c \psi_i$$

(27)

where $c = \pm 1$ in order to satisfy normalization conditions. Therefore the effect of any symmetry operation on a nondegenerate eigenfunction will be to leave it unchanged (symmetric) or change its sign (antisymmetric). The treatment of degenerate eigenfunctions is more involved and is discussed by Herzberg (8) and Kimball (2).

Herzberg has shown that symmetry operations have the same effect on non-degenerate vibrations as they

do on nondegenerate eigenfunctions, that is the vibrations are symmetric or antisymmetric with respect to any given operation.

The present information available indicates that nitrogen dioxide is a non-linear symmetrical molecule. This model has four symmetry elements or operations, for example: (see fig.1.)

(1) I - identity operation - leaves molecule unchanged.

(2) C_2 - two-fold rotation axis - rotation through 180°

(3) σ_v (xz)

(4) σ_v (yz) reflection planes passing through C_2

These symmetries belong to the point group C_{2v} for which the following tables are given by Herzberg (9) (10)

Table I

Species	I	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	Non Genuine Vibrations	
A_1	+1	+1	+1	+1	T_z	
A_2	+1	+1	-1	-1		R_z
B_1	+1	-1	+1	-1	T_x	R_y
B_2	+1	-1	-1	+1	T_y	R_x

In table I, there are four classes or species of vibrations, A_1 , B_1 , A_2 , B_2 , since the normal vibrations may be symmetric (+1) or antisymmetric (-1) with

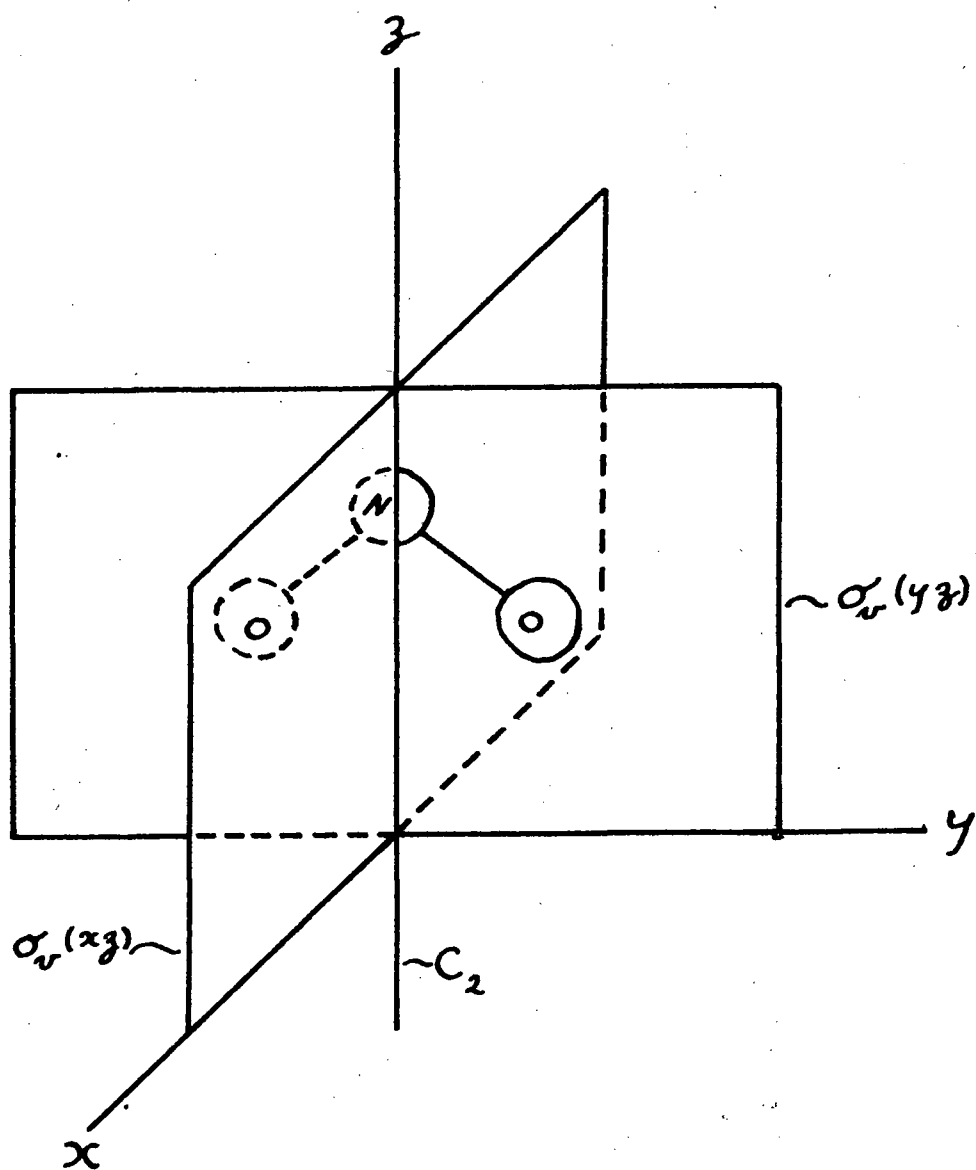


fig. 1

respect to a rotation or a reflection operation. Obviously, the vibration must be symmetric with respect to the identity operation I . In addition, the parity of the vibration in any symmetry element must satisfy the combination rules of that element with other elements. These combination rules are as follows:

$$C_2^2 = C_2 \cdot C_2 = I$$

$$\sigma_v^2(xz) = I$$

$$\sigma_v(xz) \sigma_v(yz) = C_2$$

The last column indicates to which species the non-genuine vibrations (rotations and reflections) belong. Therefore this table indicates what the four species of vibration are. For example, the first species A_1 is totally symmetric to all symmetry elements. In addition the non-genuine vibration T_z is contained in this species. In other words, Table I indicates the nature of all possible types of vibration in the molecule, but gives no information as to the number of vibrations in the molecule.

The problem of determining the number of normal vibrations belonging to each species is solved by

introducing the concept of equivalent nuclei (10). Equivalent nuclei are nuclei which are transformed into each other by the symmetry operations possible in the molecule. For example, the two oxygen nuclei in nitrogen dioxide are equivalent. If there are m sets of equivalent nuclei which do not fall on any symmetry element, these m sets will contribute $3m$ degrees of freedom to the molecule. On the other hand, if m' sets of equivalent nuclei fall on a symmetry element, these m' sets will contribute $2m'$, m' or 0 degrees of freedom, depending on the symmetry element. The use of this concept allows Table I to be reconstructed in such a way that the number of genuine normal vibrations may be found. (see Table II).

Table II

	I	C ₂	σ_v (xz)	σ_v (yz)	Non-Genuine	Genuine Vibrations
Species	on no element	on C ₂ $\sigma(xz) + \sigma(yz)$	on $\sigma(xz)$	on $\sigma(yz)$		
A1	3m	1mo	2mxz	2myz	Tz	3m + 2mxz + 2myz + mo-1
A2	3m	0mo	1mxz	1myz	Rz	3m + 2mxz + 2myz - 1
B1	3m	1mo	2mxz	1myz	Tx Ry	3m + 2mxz + myz + ^{mo - 2}
B2	3m	1mo	1mxz	2myz	Ty Rx	3m + 2mxz + 2myz + mo-2

The sets contained in no real symmetry element, are of course contained in the identity element I and therefore contribute $3m$ degrees of freedom. The m_{xz} sets contribute two degrees of freedom for symmetric vibrations since they are restricted to move in the xz plane, whereas they contribute one degree of freedom for antisymmetric vibrations since they must move perpendicularly to the xz plane (see fig.1). The m_o sets contribute one degree of freedom for symmetric vibrations since they are constrained to remain in both planes and may only move along the C_2 (z) axis.

It is apparent from figure I that:

$$m = 6$$

$$m_{xz} = 0$$

$$m_{yz} = 1 \quad (\text{two oxygen nuclei form 1 set})$$

$$m_o = 1 \quad (\text{nitrogen nucleus})$$

therefore, table III may be calculated from tables I and II.

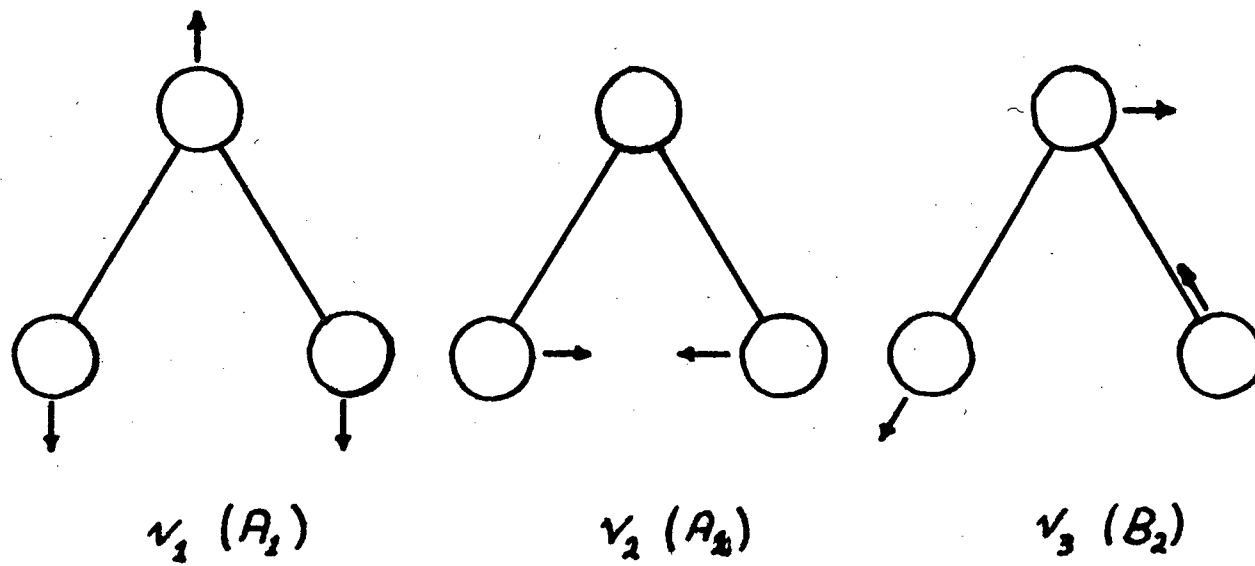


fig. 2

Table III

Species	Description			Genuine Vibrations	
	C2	$\sigma(xz)$	$\sigma(yz)$	General	NO ₂
A1	+1	+1	+1	$3m+2mxz+2myz+mo - 1$	2
A2	+1	-1	-1	$3m+mxy+mxz - 1$	0
B1	-1	+1	-1	$3m+2mxz+myz+mo - 2$	0
B2	-1	-1	+1	$3m+mxz+2myz+mo - 2$	1

From table III, it is easily verified that there are $3N-6$ internal vibrations as predicted by equation 6. These can be shown diagrammatically (see fig. 2) by applying the information in table III to figure 1.

(d) Determination of the force constants in NO₂

Now that the form of the normal vibrations with respect to the symmetry elements of the molecule has been determined, the form of the normal vibrations may be expressed in symmetry coordinates. (11) This choice of coordinates results in a considerable simplification of the secular equation which now becomes:

$$\begin{vmatrix} c_{11} - \lambda d_{11} & c_{12} - \lambda d_{12} & 0 \\ c_{21} - \lambda d_{21} & c_{22} - \lambda d_{22} & 0 \\ 0 & 0 & c_{33} - \lambda d_{33} \end{vmatrix} = 0 \quad (28)$$

The solution of this equation results in three equations which describe the frequencies of the normal vibrations.

$$\begin{aligned} \lambda_3 &= 4\pi^2 \nu_3^2 = \left(\frac{1}{m_O} + \frac{2}{m_N} \sin^2 \alpha \right) (a_{11} - a_{12}) \\ \lambda_1 + \lambda_2 &= 4\pi^2 (\nu_1^2 + \nu_2^2) = \left(\frac{1}{m_O} + \frac{2}{m_N} \cos^2 \alpha \right) (a_{11} + a_{12}) + \frac{2a_{33}}{m_O} + \frac{4a_{13}}{m_O} \sin \alpha \quad (29) \\ \lambda_1 \lambda_2 &= 16\pi^4 \nu_1^2 \nu_2^2 = \frac{2(2m_O + m_N)}{m_O^2 m_N} \cos^2 \alpha [(a_{11} + a_{12})a_{33} - 2a_{13}^2] \end{aligned}$$

where m_N and m_O are the masses of the nitrogen and oxygen atoms respectively and 2α is the ONO angle.

However, there still remain four force constants, therefore a unique solution is not possible since only three fundamental frequencies exist. Therefore in

order to estimate the value of the force constants, the assumption that only central forces exist, that is, the interatomic forces depend only on the interatomic distances. Herzberg(12) has shown that in this case;

$$a_{12} = a_{13} = a_{23} = 0, \quad a_{11} = a_{22}$$

Therefore equations 29 become:

$$\lambda_3 = \left(1 + \frac{2m_0}{m_N} \sin^2 \alpha\right) \frac{a_{11}}{m_0}$$

(30)

$$\lambda_1 + \lambda_2 = 2 \frac{a_{33}}{m_0} + \frac{a_{11}}{m_0} \left(1 + \frac{2m_0}{m_N} \cos^2 \alpha\right)$$

$$\lambda_1 \lambda_2 = 2 \left(1 + 2 \frac{m_0}{m_N}\right) \cos^2 \alpha \frac{a_{11} a_{33}}{m_0^2}$$

where ν_1, ν_2, ν_3 , are the classical frequencies of the three normal vibrations in the molecule and a_{11} and a_{33} interatomic force constants.

3. Selection Rules

From a classical point of view, if an oscillating dipole exists for any particular mode of vibration, then an infrared absorption should exist. It is apparent from diagram 1 that ν_1 , ν_2 , and ν_3 should be infrared active.

According to quantum mechanics, an infrared absorption band will occur as a result of a transition from a lower (ν') to a higher (ν'') vibrational level whenever the matrix element

$$[M] = \int \psi_{\nu''} M \psi_{\nu'} d\tau \quad (31)$$

is different from zero.

This condition can be used to show that ν_1 , ν_2 and ν_3 should be infrared active as well as the combination and difference tones of these fundamentals.

Since nitrogen dioxide will be an asymmetric rotator if the assumption that the molecule is non-linear is valid, no explicit expression for the rotational energy levels can be used. This complicates the rotational fine structure, or if the fine structure cannot be resolved, no explicit band contour for the different fundamental absorption bands can be predicted with accuracy. Dennison (1) has shown that in the case of a plane asymmetric rotator, the vibrations

may be divided into three classes according to the directions along which the dipole moment changes during the vibration. That is the change in dipole moment may be parallel to:

- (1) greatest axis of inertia
- (2) middle axis of inertia
- (3) least axis of inertia

In case 1, the absorption band may be expected to have a rather diffuse Q branch along with P and R branches. In case 2, a doublet structure should occur and in case 3, a sharp Q branch and rather weak P and R branches should occur.

It may also be shown (19) that if for a non-linear symmetrical tri-atomic molecule such as NO_2 the frequency of any combination band may be given as

$$\nu = \Delta n_1 \nu_1 + \Delta n_2 \nu_2 + \Delta n_3 \nu_3 \quad (32)$$

(anharmonicity effects being neglected), then if Δn_3 is odd, the change in electric moment will be perpendicular to the symmetry axis of the molecule.

If Δn_3 is zero or even, the change in electric moment will be parallel to the symmetry axis of the molecule.

III

EXPERIMENTAL PROCEDURE

(1) Apparatus

The Perkin-Elmer spectrometer and equipment used in the experiment is essentially the same as described by Edwards, Mitchner, and Rogers (15). A few modifications were made and these are described below:

(2) Modifications in temperature and humidity Control

1. Installation of antivibration mountings on the fan and fan housing.

2. Alteration of control circuit to give more effective control in the constant temperature box. These are:

- (a) continuous operation of the fan while the spectrometer is operating.
- (b) automatic discontinuous control of fan motor and solenoid valve by humidistat.
- (c) installation of a thermometer on the low pressure side of the evaporator coils.

It was found that the best air flow for the most efficient dehumidification could be obtained by adjusting the air flow till the temperature at this point is 4 - 6 degrees centigrade. These modifications effectively

removed all vibrations and maintained the box at a constant temperature of 68 ± 2 deg F. as well as keeping the humidity below 40% at all times.

(b) Modifications to the spectrometer

1. Installation of antivibration mountings.

The combination of both antivibration mountings on the spectrometer and the dehumidification unit apparently removed all vibration in the spectrometer.

2. Installation of a new wave drive system and an automatic calibration marker. This is described in detail in the calibration procedure.

(2) Calibration Procedure

The spectrometer was calibrated by comparing the spectra of water vapour, carbon dioxide and ammonia which were observed on our Perkin-Elmer spectrometer to the spectral diagrams of the same substances published by Oetegen et al (16). This comparison was used to develop equations relating wavelength drum readings to wave numbers.

(a) Wavelength drive and automatic calibration marker

The methods of operating the spectrometer are essentially the same as described by Mitchner et al (15). However an automatic calibration marker

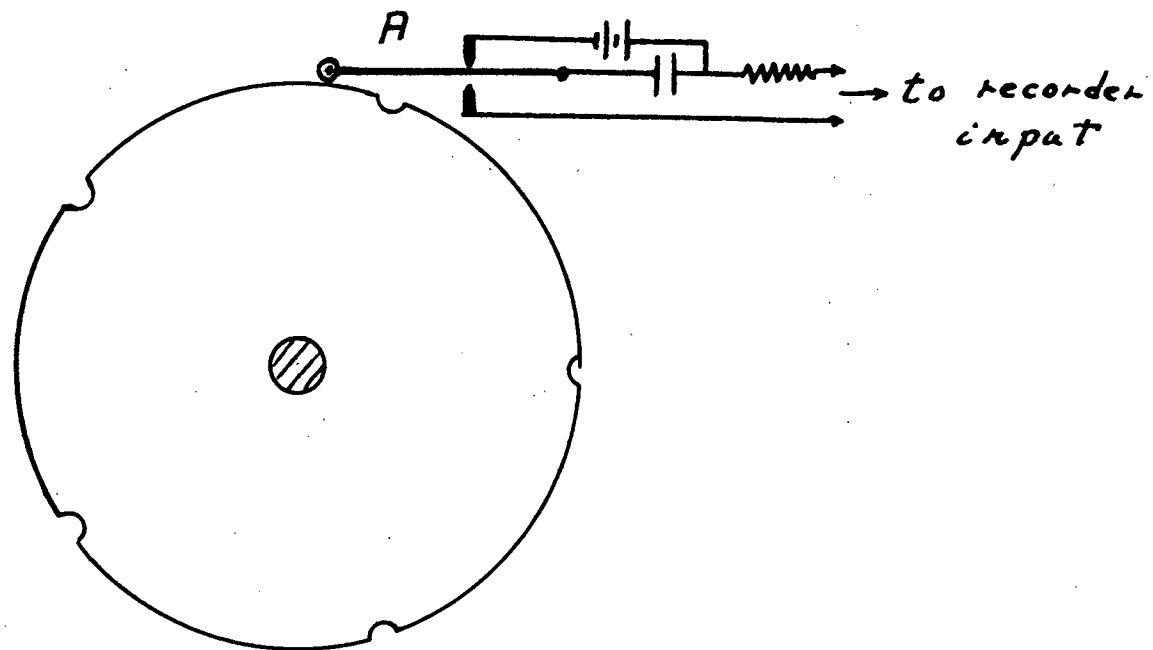


fig. 3

was added which transfers the position of the wavelength drum to the paper on the Brown recorder. The operation of this marker is shown in figure 3. This drum is mounted on the wave drive shaft and rotates with the wavelength drum. When the micro-switch A is in the up position the condenser C is charged by the battery. When the micro-switch cam falls into one of the indentations on the drum, the micro-switch closes and discharges the condenser into the Brown recorder input, thus putting a small fiducial mark or pip on the chart paper. The size and shape of these may be controlled by altering the values of the capacity and the resistance in the circuit. There are six indentations corresponding to the 0, 20, 40, 60, 80, 90, division positions on the drum. These were made with a milling machine and their angular position deviates less than 0.1 degrees from the exact position. This allows a precision of better than 0.1 divisions on the wavelength drum.

In order to drive the wavelength drive and marker drum, a wavelength drive consisting of a 2 r.p.m. Telchron clock motor and a four speed gear box which drives the drum at 1, $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{6}$ r.p.m. was built. The precision of the driving mechanism and the automatic marker was checked by measuring the

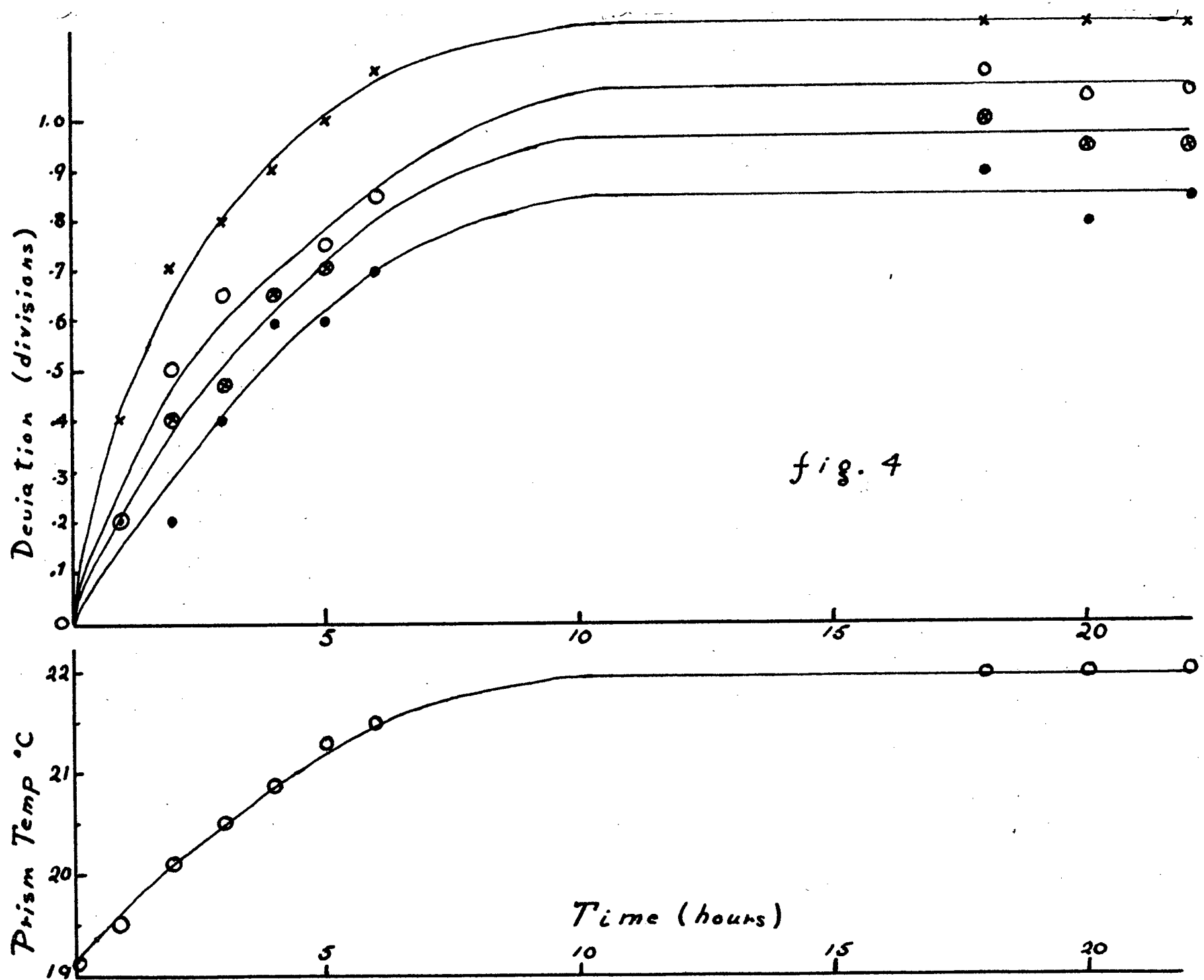
distance between successive calibration marks on a chart.

In order to check the precision of the spectrometer, the following tests were made:

- (1) variation of band position with prism temperature.
- (2) Variation of band position with varying slit width.
- (3) Variation of band position with scanning speed of wave drive.
 - (a) caused by time lag in thermocouple heating
 - (b) caused by a lower pen writing speed than scanning speed on very sharp absorption bands.
- (4) Variation of band position under 'optimum' conditions for immediately repeated runs.
- (5) Variation of band position under 'optimum' conditions for runs extending over a period of time.

(1) Variation of band position with prism temperature

A thermocouple was fastened to the back of the prism and then repeated measurements of four bands at different drum readings were taken at regular time



intervals. At the same time the temperature of the prism was measured. During this time the globalar was left on continuously, and the radiation passing into the spectrometer heated the prism. Figure 4 shows the drift from the original position of the band and the temperature rise of the prism. It was decided that before any run, the globalar should be left on for at least 12 hours, to allow the prism temperature to come to equilibrium. The conditions adopted were;

globalar power - 225 watts

slit micrometer - .330 mm.

(2) Variation of band position with slit width.

It was expected that the apparent position of an assymetric band would change with variations of slit width because the resolving power changes. However, symmetrical bands should not shift unless the exit and entrance slits do not open symmetrically. This was checked by measuring the position of a sharp symmetrical band repeatedly at different slit widths. The spectrometer was brought to equilibrium conditions as indicated in section 1. In addition, these measurements were made at the same scanning speed to eliminate any variation with scanning speed. Further-

more, the amplifier gain for each successive run was altered so that the throw of the recording pen was the same for each run. The results are as follows:

Table IV

slit width	Band #1	Band #2
.265	1501.27 (div)	1507.37 (div)
.270	1501.34	1507.55
.280	1501.34	1507.59
.290	1501.33	1507.49
.300	1501.26	1507.34
.310	1501.39	1507.24
.320	1501.34	1507.29
mean	1501.33	1507.41
$\sigma = \sqrt{\frac{(\pi - \bar{\pi})^2}{n-1}}$	0.05	0.13

This table and the average value for $\hat{\sigma}$ indicate that there is no marked change in band position with variations in slit width. The variation in band #2 might indicate that it is not quite symmetrical.

(3) Variation of band position with scanning speed

(a) An attempt to measure the thermocouple response time was made by holding all conditions con-

stant except the amplifier gain. Thus in order to trace out the same band, the recorder pen had to travel greater distances. The results are shown below:

Table V

<u>gain</u>	<u>Band #1</u>	<u>Band #2</u>
1	1501.24 (div)	1507.41 (div)
3	1501.17	1507.43
5	1501.11	1507.38
7	1501.11	1507.33
full	1501.11	1507.36
mean	1501.15	1507.38
σ	0.06	0.04

The shift towards lower drum readings appears to be significant and since this was done at the lowest scanning speed, the effect should be more pronounced for the other speeds. However, this shift is less than the overall variation discussed in section 5, therefore no attempt was made to compensate for it.

(4) Variation of band position under optimum conditions for immediately repeated runs

The 'optimum' conditions were set up as follows:

(a) the spectrometer was brought to an equilibrium temperature by operating the globar at 225 watts with the slit width set at .330 mm.

(b) sharp symmetrical bands were chosen for measurement.

(c) after setting the slit width and gain, these controls were left untouched.

(d) the slowest scanning speed, 1/6 r.p.m. was used.

(e) the measurements on the paper were made with a ruler graduated in 0.01". Estimates to the nearest 0.001" were made with an eyepiece.

(f) the whole sample of measurements were made in the shortest possible time. The results are as follows:

Table VI

	<u>Band #1</u>	<u>Band #2</u>
	1501.67	1507.87
	1501.63	1507.85
	1501.65	1507.93
	1501.60	1507.89
	1501.58	1507.89
	1501.62	1507.88
	<u>1501.64</u>	<u>1507.88</u>
mean	1501.63	1507.88
σ	0.03	0.03

(5) Variation of band position over an extended period of time.

The results of all the previous measurements which were made on the two bands at 1501 and 1507 divisions, in addition to further measurements at optimum conditions at various times, were combined with the result that an unbiased estimate for the standard deviation is

0.23 divisions.

This value is valid only for the lowest scanning speed. At higher speeds, the precision would be expected to drop inversely as the scanning speed

approximately because the separation between calibration marks decreases. The chart is driven at a constant speed, hence the percentage error in measuring rises.

Table VII

<u>Scanning speed</u>	<u>r.p.m.</u>	<u>$\hat{\sigma}$ (divisions)</u>
6	1/6	.23
4	1/4	.35
2	1/2	.66
1	1	1.5

Development of calibration formulae

The following equations have been used to correlate wave drive division numbers and wave numbers:

(1) $V = Ae^{ax} + Be^{bx}$ fitted by Prony's method

(2) $V = a + bx + cx^2 + dx^3$ fitted by Lagrange's method

(3) $x = x_0 + \frac{a}{V^2 - V_0^2}$ fitted by least squares method

(4) $V = a + bx + cx^2 + dx^3$ fitted by difference table from evenly spaced arguments of x.

Equation 3 was adopted since it was possible to fit x and a with a least squares fit. V_0 is supposedly

the reststrahlen frequency of the prism material. However, this value of ν_0 was found to be unsatisfactory. Therefore an empirical value was obtained by fitting the equation at three points and then calculating the value of ν_0 from the equations:

$$\nu_0^2 = \frac{\nu_3^2 - \nu_1^2 K}{1 - K} \quad (33)$$

$$K = \frac{x_1 - x_2}{x_2 - x_3} \cdot \frac{\nu_3^2 - \nu_2^2}{\nu_2^2 - \nu_1^2}$$

The values of x_0 and a could then be calculated by a least squares method. Table VIII gives the set of calibration constants for the NaCl prism for different ranges of the wave drive drum setting.

Table VIII

Range (div)	ν_0^2	a	x_0
250-550	.015176	-.6231750	1.770267
550-850	.026664	-.594458	1.740832
850-1150	.012373	-.620298	1.760046
1150-1450	.002039	-.629582	1.762935
1450-1650	-.033228	-.643935	1.764559

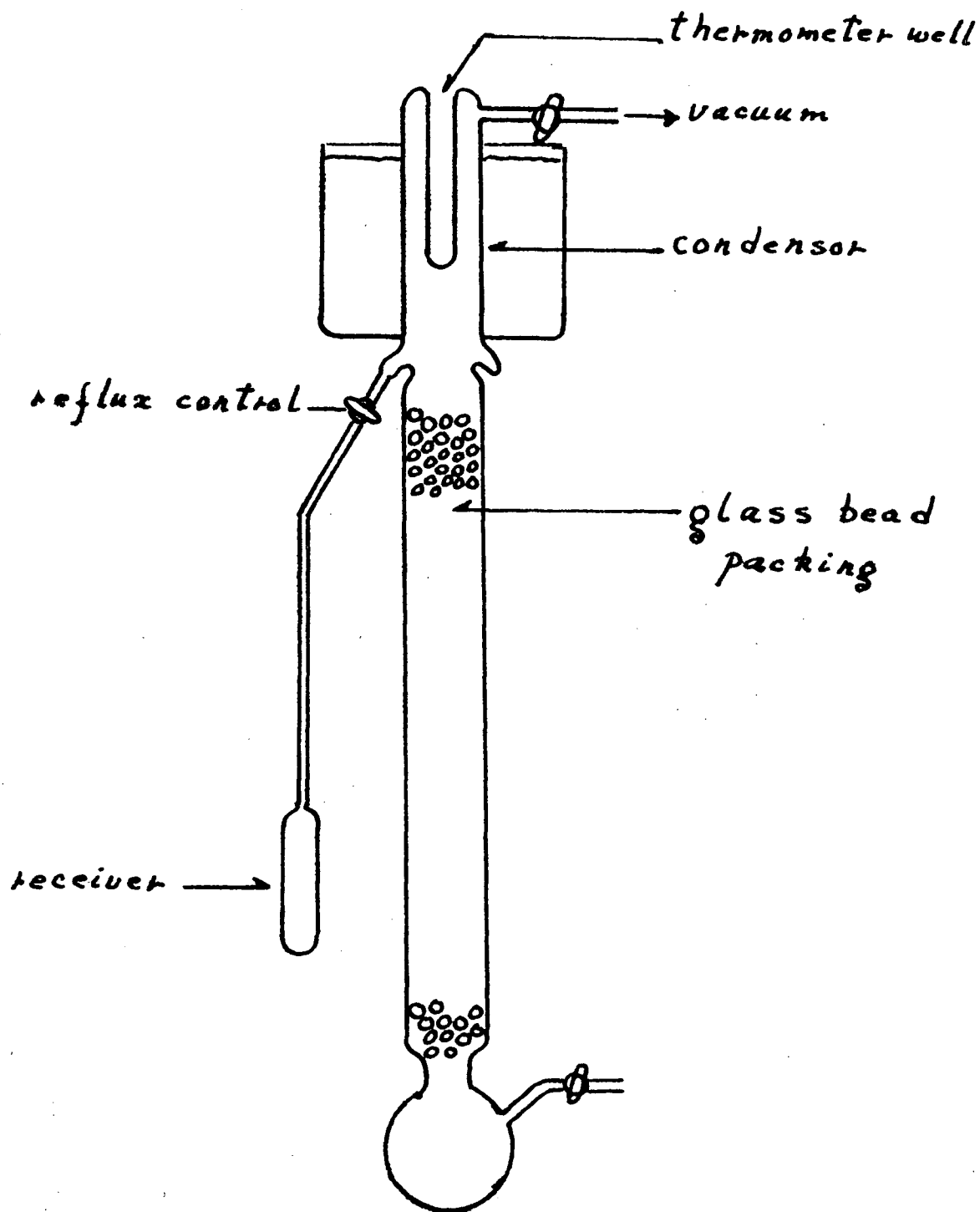


fig. 5

(3) Preparation and Treatment of the sample

A cylinder containing commercial nitrogen dioxide, nitrogen tetroxide mixture was obtained from Matheson Company. According to specifications, the purity of this product was 97%. However, initial tests showed that the first sample distilled from the cylinder contained large amounts of nitrogen trioxide (N_2O_3). The nitrogen dioxide was separated from the nitrogen trioxide and other possible impurities by distillation in the apparatus shown in figure 5. The commercial nitrogen dioxide was distilled from the cylinder to the distilling pot by cooling the pot in ice and water after the whole system had been previously dried and evacuated and then sealed off from the vacuum pump. After collecting about 250 ccs., the filling tube was sealed off. During distillation the condenser jacket was filled with dry ice and the distilling pot was heated to 23 - 28 deg. C., while the receiver was cooled in an ice and water mixture. The reflux was controlled by adjusting the stop cock connected above the receiver. This was adjusted until the reflux ratio was about 3 to 1.

The reflux was very difficult to control because the whole system was sealed. This condition allowed pumping from the receiver to the condenser or from the

condenser to the receiver depending on their relative temperatures. This could have been prevented by bringing both the condenser and receiver to atmospheric pressure by opening them to the air through potassium hydroxide drying tubes. However, a fume hood was not available, and it was found that potassium hydroxide did not remove the nitrogen oxides rapidly enough to make this procedure feasible without a fume hood as a precaution.

Unfortunately, the boiling point of the different fractions was not obtained because the pressure in the condenser was not known. Therefore the course of the distillation was followed by observing the change in colour of the distillate. The first fraction, approximately 100 ccs. was a light green liquid, which solidified to a mass of bright blue and white crystals. Since N_2O_3 is a blue liquid (B.P. 3.5 deg C.) which solidifies to a blue solid (M.P. -104 deg C.) and N_2O_4 is a brownish liquid (B.P. 21.3 deg C.) which solidifies to a colourless solid (M.P. -9.3 deg C.), this first fraction was considered to be N_2O_3 with N_2O_4 as an impurity. An intermediate fraction of about 50 ccs was removed and discarded. The third and fourth fractions, each about 20 ccs, were a light brown liquid. Each solidified to a colourless solid containing a slight

amount of orange coloured impurity, (approximately 1% of the total volume). Since none of the oxides of nitrogen are this colour in the solid state, it was assumed that this impurity was some reaction product of the nitrogen tetroxide and the stopcock grease used in the reflux control stopcock. No attempt was made to remove this as stopcocks could not be eliminated from the apparatus.

The freezing point of the sample was found to be -11 deg C. This was determined by freezing the liquid in a sealed cell, using a copper constantin thermocouple.

(4) Design of the Absorption Cell and Gas Filling Apparatus

In view of the fact that NO_2 and N_2O_4 are highly reactive with practically all substances except glass, the apparatus shown in figure 6 was designed to eliminate contact of the vapour with the most important foreign substance, water vapour. The absorption cell was made by attaching a stopcock to an 11 cm piece of glass tubing, the ends of which were ground flat, so that two polished rock salt windows could be attached with glyptal cement. The outside of the cell was wound with a 70 ohm heating element which was covered with asbestos insulation. For temperature measurement, a

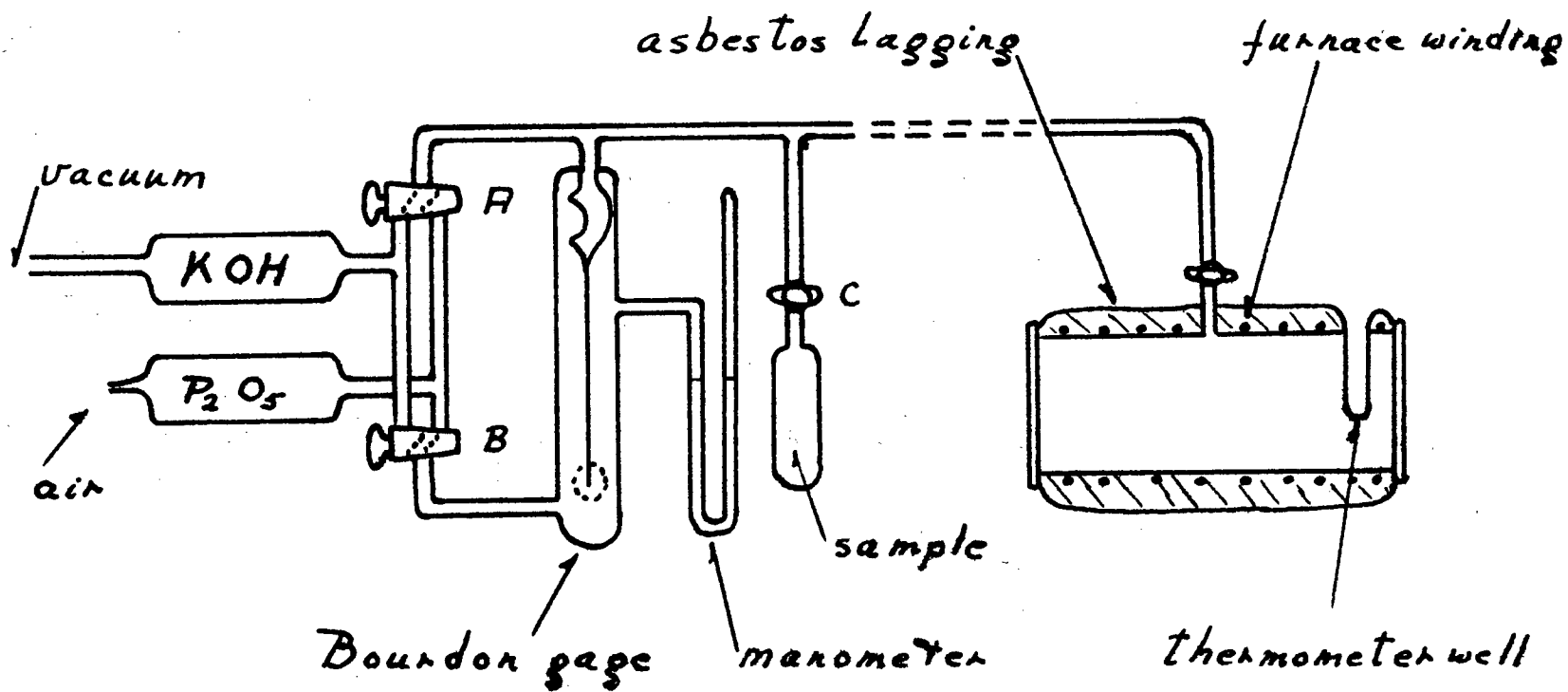


fig. 6

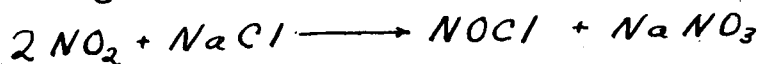
thermometer well was placed in the cell in such a position that it did not obstruct the optical path.

With this arrangement, it was possible to evacuate the cell and fill it with dry air if necessary, or fill it with NO_2 at will by manipulation of the three-way stopcocks A and B (see fig.6). Filling the cell was accomplished by first evacuating the whole system, closing stopcock A and filling the outer chamber of the Bourdon gage with dry air to the required pressure which was measured on the mercury manometer. Stopcock C was opened and NO_2 vapour passed into the cell and the inner part of the Bourdon gage. When the pressure of NO_2 vapour was equal to the pressure of the air in the outer bulb, the pointer on the Bourdon gauge returned to the same null position as it indicated when both sides were under vacuum. This null position was determined by observing the pointer with a low power microscope, (approximately 100x) fitted with a micrometer eyepiece. The sensitivity of the gage was 0.15 mm./cm. of Hg. In practise the pointer was very subject to vibration and this made the null readings very difficult to obtain. However, pressure measurements were made only to the nearest millimeter of Hg and the gage proved to be quite satisfactory for this purpose.

This arrangement excluded the introduction of all possible impurities but three. These are:

- (1) reaction products of NO_2 with stopcock grease.
- (2) reaction products of NO_2 with the glyptal cement attaching the windows to the absorption cell.
- (3) reaction products of NO_2 with the NaCl windows in the absorption cell.

Both the glyptal and the stopcock grease are hydrocarbons which would be nitrated by NO_2 to form a non-volatile compound. However, there may also be some gaseous by-product in the reaction. In practise, it was found that the glyptal was attacked only slightly, if at all, but the stopcock grease was attacked very rapidly. The third possibility involves the following reaction:



Taraskina and Didusenko (22) state that this reaction is catalysed by the presence of water. Hence the cell was carefully heated to about 130 deg C. and pumped to remove any absorbed water vapour. It was found that increased temperatures increased the rate of reaction also. Fortunately, evidence of the reaction could easily be obtained by measuring the intensity of the NaNO_3 band at 1363 cm^{-1} .

IV

RESULTS

Since the samples of NO_2 which were prepared were not completely pure, the following criterion was adopted for the assignment of the absorption bands in table IX:

(1) Bands which increase in intensity as the temperature rises, and return to their original intensity when the cell is returned to its initial temperature, belong to NO_2 .

(2) Bands which decrease in intensity as the temperature rises, and return to their original intensity when the cell is returned to its initial temperature belong to N_2O_4 .

(3) Bands whose intensities are independent of temperature belong to impurities introduced with the sample.

(4) Bands which increase in intensity with time, belong to impurities produced by the reaction of the NO_2 with the stopcock grease, NaCl window, or with the glyptal cement.

Table IX

<u>NO₂ (cm⁻¹)</u>	<u>N₂O₄ (cm⁻¹)</u>	<u>NO₃⁻ (cm⁻¹)</u>
1312 weak	751 vvs	835 weak
1601 vvs	1013 v weak	1363 vvs
2898 s	1263 vs	
3555 m	1926 vvs	
4180 v weak	2583 m	
4750 v weak	2632 s	
	2971 s	
	3114 m	
	3437 v weak	
	4672 v weak	

The bands at 2898, 4180 and 4750 cm⁻¹ were resolved as follows in table X:

Table X

<u>band</u>	<u>type</u>	<u>PR separation</u>
2898	2888 2895 2916	PQR 28 cm ⁻¹
4180	4164 4197	doublet 33 cm ⁻¹
4750	4736 4765	doublet 29 cm ⁻¹

The resolution of the band at 1601 cm^{-1} was incomplete, but it appeared to be a doublet. It was impossible to determine whether the band at 1312 cm^{-1} was resolved or not, since it was badly obscured by the NO_3^- band at 1363 cm^{-1} .

Electron diffraction data (14) gives the ONO band angle as 130° and the NO bond distance as 1.20 \AA . This data gives the following moments of inertia for the molecule

$$\begin{aligned} I_A &= 4.19 \times 10^{-40} \text{ gm cm}^2 \\ I_B &= 62.9 \times 10^{-40} \text{ " " } \\ I_C &= 67.1 \times 10^{-40} \text{ " " } \end{aligned}$$

where I_B is the figure axis of the molecule. Since $I_B \simeq I_C$, the molecule can be considered as a symmetric top and the doublet spacing can be calculated from Dennison's formula (4).

$$\Delta \nu = \frac{S(\beta)}{\pi} \sqrt{\frac{kT}{A}} = 12.5 S(\beta) \sqrt{\frac{T}{A}}, \text{ cm}^{-1}$$

$$A' = A \times 10^{40}$$

$$\log_{10} S(\beta) = \frac{0.721}{(\beta + 4)^{1.13}}$$

$$\beta = \frac{A}{C} - 1$$

$$A \simeq \frac{I_B + I_C}{2}, \quad C = I_A$$

The doublet spacing as calculated above is 28 cm^{-1} , which agrees with the observed spacings in table X.

Since the fundamentals ν_1 and ν_2 belong to the A_1 type vibration, the electric moment of the molecule can only change parallel to the figure axis of the molecule; that is, along the middle axis of inertia of the molecule I_B . Therefore ν_1 and ν_2 should have a doublet contour, whereas the electric moment varies parallel to the least axis of inertia I_A in the vibration ν_3 which would be expected to have a PQR contour.

The selection rules for combination tones (see page 27) show that any overtone formed from odd multiples of ν_3 should have a PQR contour, and all others should possess a doublet contour. The assignment below using 648 cm^{-1} which was observed by Sutherland (20) seems to satisfy the selection rules for band contours:

Table XI

Assignment	observed		calculated	
	cm ⁻¹	contour	cm ⁻¹	contour
ν_2 (A_1)	648	doublet		doublet
ν_3 (B_2)	1312	Q branch?		PQR
ν_1 (A_1)	1601	doublet?		doublet
$\nu_3 + \nu_1$ (B_2)	2898	PQR	2913	PQR
$\nu_1 + \nu_2 + \nu_3$ (B_2)	3555	Q branch	3561	PQR
$2\nu_3 + \nu_1$ (A_1)	4180	doublet	4225	doublet
$3\nu_1$ (A_1)	4750	doublet	4803	doublet

The main weakness with this assignment is the absence of $2\nu_1$, and $2\nu_3$. However, the bands at 3114 and 2632 cm⁻¹ which have been assigned to N₂O₄ may well be due to both NO₂ and N₂O₄. The validity of this assumption could be checked by examining the temperature dependence of these bands quantitatively. As yet, this has not been done.

Using the above assignment, the equations 30 may be solved for a_{11} and a_{33} and the ONO bond angle 2α . The force constants are:

$$f_{NO} = a_{11} = 9.30 \times 10^5 \text{ dynes/cm}$$

$$f_{OO} = a_{33} = 2.30 \times 10^5 \text{ dynes/cm}$$

and the ONO bond angle is 145°.

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