

The Infrared Absorption Spectra of Nitrogen Dioxide and Tetroxide

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The Infrared Absorption Spectra of Nitrogen Dioxide and Tetroxide*

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The absorption spectra from 1 to 4μ of pure NO_2 - N_2O_4 mixtures in a long tube were examined with a rocksalt and a quartz spectrometer. Several new bands were discovered from 1.9 to 4μ in the spectra of both NO_2 and N_2O_4 . The NO_2 bands were analyzed as combinations of two fundamentals. The N_2O_4 bands were interpreted as combinations and harmonics of reported fundamentals. Three bands of

N_2O_4 lie at shorter wave-lengths than correspond to the work of dissociation into 2 NO_2 . A study of the symmetry properties shows that only those models where the NO_2 groups are joined by the nitrogen atoms would give rise to the observed infrared spectrum. Some features of the spectrum seem to be in favor of the existence of molecules where the NO_2 groups do not lie in the same plane.

INTRODUCTION

THE infrared absorption spectrum of the NO_2 - N_2O_4 system has recently been investigated by several authors.^{1, 2, 3, 4} We present in this paper the absorption spectrum, in the nearer infrared, of deep layers of some very pure NO_2 and N_2O_4 ,⁵ as resolved by a rocksalt and by a quartz prism spectrometer. The spectrum of N_2O_4 in this region is composed of distinct bands which we consider to be combinations of the fundamentals reported by Sutherland.^{1, 6} Two bands of NO_2 are discovered which we have interpreted as combinations of some undiscovered fundamental with one already known.

* Contribution No. 319.

¹ G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 342 (1933).

² R. Schaffert, J. Chem. Phys. **1**, 507 (1933).

³ A. B. D. Cassie and R. L. Bailey, Nature **131**, 239 (1933).

⁴ J. Strong and T. Woo, Phys. Rev. **42**, 267 (1932).

⁵ The preparation will be described elsewhere by L. Harris and W. S. Benedict.

⁶ G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 535 (1933).

APPARATUS

Since the gases react with cements, metals and greases, they were confined in an all quartz absorption tube 100 cm long and 2.54 cm diameter, surrounded by an electric furnace. The windows were of carefully selected quartz and, although only 2.0 mm thick, were opaque beyond 4μ .

In order to reach this wave-length no other quartz was permitted in the optical path, in one series of experiments. The light of a Nernst glower was reflected by gold mirrors through the tube and then through a minimum deviation 60° rock-salt prism spectrometer. A Coblentz twenty-two junction thermopile traversed the spectrum with twice the angular velocity of the prism and the angle of (minimum) deviation of the incident light was measured by a graduated table reading to five seconds. This spectrometer was calibrated by the simple minimum deviation formula. Paschen's⁷ values for the refractive index of rock-salt corrected to 21°C were used but so few points are given in this region of inflection that a considerable uncertainty in the wave-length arises

⁷ Paschen, Ann. d. Physik [4] **26**, 120, 1029 (1908).

($\pm 0.003\mu$). The prism was kept at constant temperature within 0.1°C since $d\lambda/dt = 0.015\mu/\text{degree}$.

In the region of transparency of quartz ($< 2.8\mu$) much higher dispersion was obtained by means of a quartz half-prism constant deviation spectrometer of large aperture. The light of a 1000 watt tungsten lamp was passed through the meter tube by quartz lenses. Monochromatic light from the exit slit was focussed on a Kipp thermopile. A graduated drum measured the angle between the half prisms in radians but the constants of the calibration had to be evaluated by locating mercury emission lines (to 1.71μ). Calibration from the positions of the bands of common substances did not seem advisable as the values in the literature do not agree.

With each instrument the positions of the absorption bands of water-vapor⁸ in the air and of three NO_2 and N_2O_4 bands⁹ agreed well within the experimental error of 0.012μ with the published values.

The intensity of the transmitted light was measured by the thermopiles and a Leeds and Northrup HS galvanometer, giving reproducible transmission curves within one percent. Two to ten readings were taken per slit width (see figures) and the curves determined several times at each absorption band. The tube was emptied by freezing out the contents into a side arm with "dry ice" (commercial solid CO_2). The transmission of the full tube was found at 21°C and 130°C with the rocksalt instrument and at 24°C and 160°C with the quartz, where the calculated compositions were as follows:¹⁰

Temperature of absorption tube ($^\circ\text{C}$)	21	24	120	130	160
Temperature of reservoir ($^\circ\text{C}$)	21	24	-12	50	75
Partial pressure reduced to 0°C					
of $\text{NO}_2(P_{\text{NO}_2})$ mm Hg	188	217	188	1034	1184
of $\text{N}_2\text{O}_4(P_{\text{N}_2\text{O}_4})$ mm Hg	511	495	2	86	12

TREATMENT OF DATA

Although we are not primarily interested in the magnitudes of the absorption coefficients, it is

⁸ G. Hettner, Ann. d. Physik [4] 55, 476 (1918).

⁹ See tables below.

¹⁰ M. Bodenstein, Zeits. f. physik. Chemie 100, 68 (1922).

necessary to resolve the absorption curve for each equilibrium mixture into its two components in order to locate the bands of each constituent. Using logarithms of transmissions, a correction was applied throughout the spectrum to the absorption curves (rocksalt data) of the mixtures by subtracting the absorption due to the minor constituent, calculated by Beer's law from the absorption curve of the other mixture where this species was now in excess. It was assumed that the absorption coefficients do not depend on the temperature or pressure under this resolution; later experiments with NO_2 showed Beer's law was valid within our experimental error, as might be expected from the fact¹ that the fundamentals even under high resolution show no detailed structure.

With the quartz spectrometer, the absorption tube was heated to 160°C , where the gas was practically pure NO_2 , so that no correction was applied for the absorption of the small amount of N_2O_4 present. To find the absorption of pure N_2O_4 we had first to estimate the absorption of the NO_2 in the gas mixture at 24°C by another series of measurements made with the tube at 120°C and the reservoir at -12° where the gas was all NO_2 , and at the same pressure as in the mixture at 24°C .

Fig. 1 shows the curves for NO_2 at 130°C and N_2O_4 at 21°C as obtained with the rocksalt spectrometer. Fig. 2 gives the absorption of NO_2 at 160°C and N_2O_4 at 24°C under the higher dispersion, all curves having been corrected as outlined above. A comparison shows how the apparent absorption increases with the resolution and how overlapping bands shift the maxima.

RESULTS

The absorption coefficients of NO_2 from 1 to 2.1μ and of N_2O_4 from 0.75 to 1.9μ are less than $0.0003 \text{ atm.}^{-1}\text{cm}^{-1}$ (three percent being the accuracy of measurements of weak absorption), unless there are bands narrower than the slit width (shown in figures). The spectra of both gases between 1.9 and 4μ consist of more or less isolated bands whose maxima are given in Tables I and II.

We use Mecke's notation, which is identified with the notation Sutherland used for the fundamentals in a later table. If the z -axis be taken

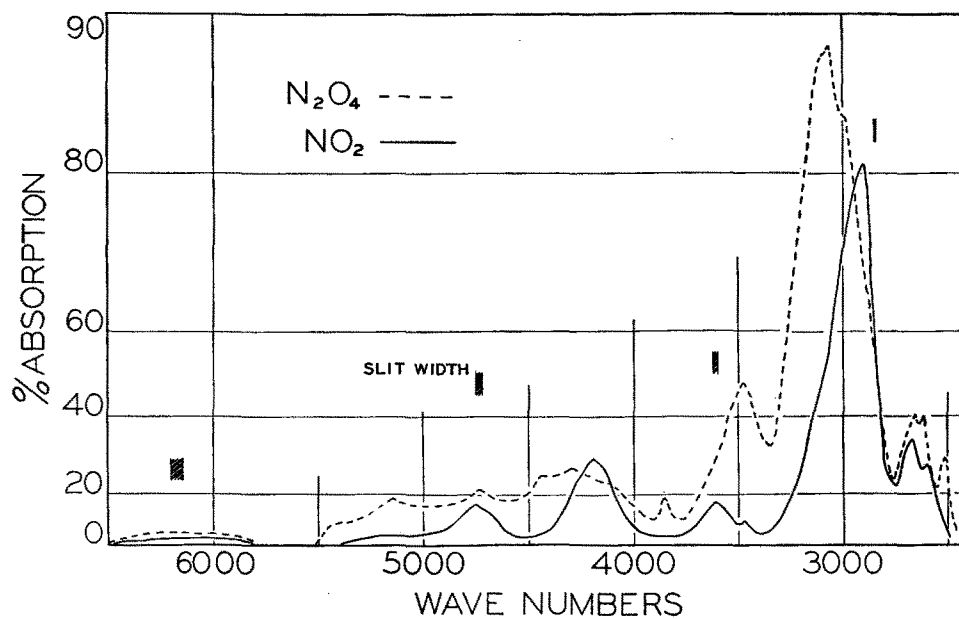


FIG. 1.

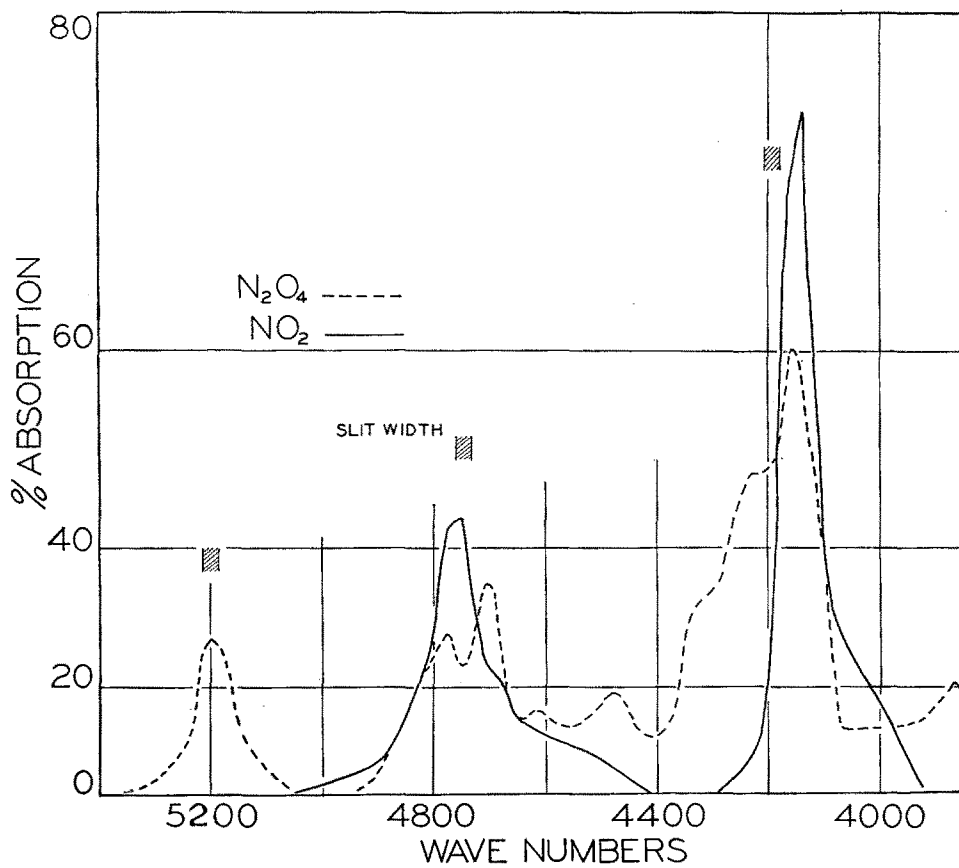


FIG. 2.

TABLE I. NO_2 at 130° and 160°C .

Observed here cm^{-1}	Observed by others cm^{-1}	Calculated cm^{-1}	Analysis	Intensity
	648 ^{1, 2, 3}	—	δ_π	Strong
	(1321) ⁵	1321	ν_π	—
	1621 ^{1, 2, 3}	1621	ν_σ	Very strong
	2220 ¹	2236	$\nu_\sigma + \delta_\pi$	Medium
{ 2601				
{ 2667	2630 ⁵	2630	$2\nu_\pi$	Medium
2905	2910 ¹	2893	$\nu_\sigma + \nu_\pi$	Very strong
ca. 3200	3242 ¹	3206	$2\nu_\sigma$	No maximum but strong absorption
{ 3454				
{ 3597		3540	$\nu_\sigma + \nu_\pi + \delta_\pi$	Weak
ca. 3930		3927	$3\nu_\pi$	Hidden weak maximum
4140		4151	$\nu_\sigma + 2\nu_\pi$	Strong
4560		4427	$2\nu_\sigma + \nu_\pi$	Hidden weak maximum
4753		4753	$3\nu_\sigma$	Medium

TABLE II. N_2O_4 at 21° and 24°C .

Observed here cm^{-1}	Observed by others cm^{-1}	Calculated cm^{-1}	Analysis	Intensity
	380 ⁴	—	$\delta_{\sigma a}$	—
	682 ¹	—	$\delta_{\sigma' a}$	—
	752 ¹	—	$\delta_{\pi a}$	—
	880 ⁴	880	$\delta_{\sigma a} + \delta_{\sigma s}$	—
	948 ¹	965	$\nu_{2\pi s} + \delta_{\sigma' a}$	—
	1265 ¹	—	$\nu_{\pi a}$	—
	1744 ¹	—	$\nu_{\sigma a}$	—
	1750	1765	$\nu_{\pi a} + \delta_{\sigma s}$	—
		2078	$\nu_{\pi a} + \delta_{\pi s}$	—
	2060 ¹	2087	$\nu_{\pi s}(2) + \delta_{\pi a}$	—
		2135		—
		(2476)	$\nu_{\sigma s} + \delta_{\pi a}$	—
	2501	2557	$\nu_{\sigma a} + \delta_{\pi s}$	Medium
{ 2608		2602		Strong
{ 2649	2620 ¹	2650	$\nu_{\pi a} + \nu_{\pi s}(2)$	Strong
{ 2967	2975 ¹	2989	$\nu_{\sigma s} + \nu_{\pi a}$	
		3009	perp. $\nu_\sigma + \nu_{\pi a}$	Very strong
{ 3077		3081		
{ 3091		3129	$\nu_{\sigma a} + \nu_{\pi s}(2)$	
3478		3468	$\nu_{\sigma a} + \nu_{\sigma s}$	Strong
		3488	perp. $2\nu_\sigma$	
		(3795)	$3\nu_{\pi a}$	
3861		3985*	$2\nu_{\pi s} + \nu_{\pi a}$	Weak
4160		4274*	$\nu_{\sigma a} + 2\nu_{\pi a}$	Strong
4230		4349*	$\nu_{\sigma s} + \nu_{\pi a} + \nu_{\pi s}$	Medium
4340		4464*	$\nu_{\sigma a} + 2\nu_{\pi s}$	Weak
4478		—	—	Weak
4620		4713*	$2\nu_{\sigma s} + \nu_{\pi a}$	Weak
		4753*	$2\nu_{\sigma a} + \nu_{\pi a}$	
4706		4753*	perp. $2\nu_\sigma + \nu_{\pi a}$	Medium
		4828*	$\nu_{\sigma a} + \nu_{\sigma s} + \nu_{\pi s}$	
4778		4848*	perp. $2\nu_\sigma + \nu_{\pi s}$	Medium
		5192	$2\nu_{\sigma s} + \nu_{\sigma a}$	
5197		5232	$3\nu_{\sigma a}$ or $3\nu_\sigma$	Medium

* Anharmonicity correction (not attempted) would justify this assignment.

through the N—N bond, then π signifies \parallel to z ; σ , \perp to z ; σ' , \perp to z and \perp to the plane of the NO_2 groups; the vibrations of the NO_2 groups will be symmetric (s) or antisymmetric (a) with respect to the center of symmetry. The assignment is for the plane molecule; for the perpendicular model the assignment is the same, except that the (σs) and (σa) vibrations become identical, as will be discussed below.

THE SPECTRUM OF NO_2

Only two fundamentals have been reported for NO_2 , at 1621 and 648 cm^{-1} .^{1, 2, 3} If the molecule is linear the third frequency ν_π can be calculated to be about 1000 cm^{-1} and although the fundamental would be absent in the infrared, combinations should be expected. The absence of a third frequency however is not a definite indication of a linear molecule; there are several triangular molecules known where the ν_π frequency appears very weakly. Harris and Benedict⁵ have found separations in the ultraviolet spectrum of NO_2 of 1321 and 2630 cm^{-1} , which are very reasonable values for ν_π , $2\nu_\pi$ of a triangular molecule. These values fit the infrared data very much better than a calculated 1000 cm^{-1} . If ν_π is weak, the other π overtones, $\nu_\sigma\nu_\sigma$, $\nu_\sigma\nu_\sigma + \nu_\pi$, etc., (ν_σ even) will also be weak (cf. H_2O ,¹¹). Table I shows that indeed the only strong bands are the σ -bands of odd ν_σ , their sharpness warranting the evaluation of three anharmonicity terms. The frequencies were calculated from

$$E = 1681(\nu_\sigma + \frac{1}{2}) + 1357(\nu_\pi + \frac{1}{2}) - 18(\nu_\sigma + \frac{1}{2})^2 - 6(\nu_\pi + \frac{1}{2})^2 - 48(\nu_\sigma + \frac{1}{2})(\nu_\pi + \frac{1}{2}).$$

The intensity of $\nu_\sigma + \nu_\pi$ and $\nu_\sigma + 2\nu_\pi$ is reflected in the magnitude of the interaction constant, -48 cm^{-1} .

Bands reported^{1, 2} at 1350–75 cm^{-1} are probably the frequency 1365 cm^{-1} of nitrite ions¹ formed by reaction of the gases with the rocksalt windows, avoided in the present work. These bands may have masked the weak NO_2 fundamental at 1321 cm^{-1} .

THE SPECTRUM OF N_2O_4

The new bands between 1 and 4μ can be satisfactorily interpreted as combinations of the re-

¹¹ Mecke *et al.*, *Zeits. f. Physik* **81**, 313 *et seq.* (1933).

TABLE III.

Representation	Operators								Configurations
	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	C_i	$C_2(z)$	$C_2(y)$	$C_2(x)$	
A_{1s}	1	1	1	1	1	1	1	1	Zero state $\nu_{\pi s} = \nu_2 = 1337$ $\delta_{\pi s} = \nu_4 = 813$ $\nu_{2\pi s} = \nu_8 = 283$ Free rotation ν_7
A_{1a}	1	1	1	1	-1	-1	-1	-1	$Z, \nu_{\pi a} = \nu_1 = 1265$ $\delta_{\pi a} = \nu_3 = 752$ $\delta_{\sigma' s} = \nu_{12}$
A_{2s}	1	1	-1	-1	1	1	-1	-1	
A_{2a}	1	1	-1	-1	-1	-1	1	1	
B_{1s}	1	-1	1	-1	1	-1	1	-1	$Y, \nu_{\sigma a} = \nu_5 = 1744$ $\delta_{\sigma a} = \nu_9 = 380$ $\nu_{\sigma s} = \nu_6 = 1724$ $\delta_{\sigma s} = \nu_{10} = 500$
B_{1a}	1	-1	1	-1	-1	1	-1	1	
B_{2s}	1	-1	-1	1	1	-1	-1	1	
B_{2a}	1	-1	-1	1	-1	1	1	-1	$X, \delta_{\sigma' a} = \nu_{11} = 682$

ported infrared and Raman fundamental frequencies. As was the case with the data treated by Sutherland, the comparative scarcity of bands in this region (if combinations and overtones of all twelve fundamentals appeared the absorption at the present dispersion would appear nearly continuous) is positive evidence for a symmetrical N₂O₄ molecule, undoubtedly one where the NO₂ groups are joined by the nitrogen atoms. However, we must examine the data for indications of two well-populated configurations of N₂O₄ of nearly the same energy, in which the NO₂ groups lie in the same plane or are mutually perpendicular, and for indications of free rotation through both these positions upon surmounting a comparatively low hill of potential energy.

Neglecting for the present the interaction with free rotation, the other eleven fundamental frequencies may be arranged among the various representations of the symmetry groups corresponding to the equilibrium positions. The selection rules of combination, derived from symmetry considerations,^{12, 13} are equally rigorous for the two configurations and are equally compatible with the observed spectra.

Plane N₂O₄ has the symmetry properties of group V_h which has the irreducible operators and representations given by Table III; the z -axis is chosen as the N—N bond; the y -axis lies perpendicular to this in the plane of the molecule.

The selection rule for the infrared, namely

$$\int (\partial m / \partial q_i) \psi_{\text{init.}}(\xi) \bar{\psi}_{\text{final}}(\xi) d\xi$$

must be positive in all symmetry operations.

¹² L. Tisza, Zeits. f. Physik **82**, 48 (1933).

¹³ R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

TABLE IV.

Representation	Operators					Configurations
	E	$C_2(z)$	$2C_2C_4, -4(z)$	$2C_2(x, y)$	$2C_2'(x', y')$	
A_1	1	1	1	1	1	Zero state $\nu_{\pi s} = 1360$ $\nu_{2\pi s} = 283$ $\delta_{\pi s} = 813$
A_2	1	1	1	-1	-1	Free rotation $\nu_{\pi a} = 1260$ $\delta_{\pi a} = 752$
B_1	1	1	-1	1	-1	
B_2	1	1	-1	-1	1	
E_0	2	-2	0	0	0	$X, Y,$ $\nu_{\sigma} = 1744$ $\delta_{\sigma} = 500 \sim 382$ $\delta_{\sigma'} = 682$

Applied to this group, it shows that for transitions from the zero state (1) no fundamentals of symmetrical (s) vibrations, or (2) even overtones of any fundamental are active and (3) there are no combinations of s with s or of a with a or (4) of vibrations lying in representations with the first subscript the same. The most intense of the permitted combinations have been given in Table II.

The perpendicular molecule is of the V_d group, described by Table IV.

The outstanding difference between the groups is seen to be the occurrence in V_d of the degenerate representation E_0 , wherein the 6 σ -vibrations coalesce to form three (not two as stated by Sutherland) degenerate pairs, which are all active. However, as only the three (σa) are active in V_h , there will be the same number of observable infrared fundamentals as in V_d . That the values of the Raman frequencies⁶ do not coincide with those of the infrared for these pairs cannot be taken as evidence against the existence of the perpendicular form in the gas, as the Raman spectrum was obtained only in the solid, which x-ray studies¹⁴ have shown to be composed of predominantly plane molecules. In the overtones and combination bands also, V_d gives the same number of active bands as V_h . In V_d , even-numbered harmonics of the σ -vibrations will occur (with pronounced Q branches) but with less than the full intensity expected of states of increased (degenerate) weight, since the characters of the product, E_0^2 , split into the sum $A_1 + B_1 + B_2$, of which only the last is active, the representation of the Z -moment. All combinations of the σ -vibrations with each other and with other types of vibrations are also permitted.

¹⁴ S. B. Hendricks, Zeits. f. Physik **70**, 699 (1931).

Throughout, a correlation of the permitted combinations of V_d with V_h may be made.

In Table II we have shown how the permitted combinations, on either model, account for the main features of the spectrum. The following considerations, however, lead us to suspect that both models participate in giving the observed bands.

The point at issue is whether the σ -vibrations have one frequency or two. Only ν_σ is observed with certainty in overtones and combinations. In the region of 1750 cm^{-1} the envelope of absorption as observed by Sutherland is wide and asymmetrical with a deep minimum which Sutherland interpreted as the central gap to be expected in the fundamental $\nu_{\sigma a}$ where the moment vibrated along the middle axis of inertia of an asymmetrical top and hence as evidence for the plane molecule. A rough calculation with the aid of Dennison's diagrams^{15, 16} reveals, however, that for a molecule as heavy as N_2O_4 the central gap would not be so wide as observed and that in all probability the envelope, under the attainable resolution, would appear with a wide and weak central maximum (ratio of moments 1 : 1.8 : 3.1). In the perpendicular model, N_2O_4 is a symmetrical top (ratio 1 : 2.6 : 2.6) and would have a somewhat stronger central maximum. It is therefore probable that the observed absorption is due to the fundamental $\nu_{\sigma(a)} = 1744\text{ cm}^{-1}$, on which is superposed the permitted combination $\nu_{\pi a} + \delta_{\sigma(s)} = 1765\text{ cm}^{-1}$. The Raman frequency of the solid (plane) occurs at 1724 cm^{-1} ; hence we must look for combinations of 1744 and 1724 from the plane and for combinations of 1744 only from the perpendicular molecules; if rotational oscillation is present the bands will lie between these limits. In the region of the fundamental the presence of weak asymmetric absorption lying to shorter frequencies of 1744 may be due to the 1724 ($\nu_{\sigma s}$) coupling with ν_{rot} to become weakly active.

The first "overtone" would lie at 3468 cm^{-1} (less some anharmonicity term which must be present if the band is to appear with appreciable intensity) if plane, and at 3488 cm^{-1} if perpendicular. The observed band at 3478 cm^{-1} is presumably the center of the overlapping of a plane

model combination, $\nu_{\sigma a} + \nu_{\sigma s} = 3468\text{ cm}^{-1}$ with the perpendicular frequency $2\nu_\sigma = 3488\text{ cm}^{-1}$.

The calculated separation between $2\nu_{\sigma(a)} + \nu_{\pi a}$ and $\nu_{\sigma(a)} + \nu_{\sigma(s)} + \nu_{\pi s}$ is 75 cm^{-1} for the plane, 95 cm^{-1} for the perpendicular molecule. The observed is $70 \pm 5\text{ cm}^{-1}$ but a correction for slit-width would increase this value. Moreover the envelope at 4778 cm^{-1} seems to be composed of the bands of both types of molecules.

All these facts are evidence for the existence of an appreciable fraction of molecules in the gas in which the NO_2 groups do not lie in the same plane. It would be of interest to examine the envelopes of these overtone bands under high resolution in the attempt to decide whether the plane or the perpendicular form is the equilibrium position of the gaseous N_2O_4 molecule and to determine the height of the potential hill hindering free rotation. However, the discussion we have given should make it clear that an unambiguous decision will be attended with difficulties.

As the single N—N bond should have no directional properties and the forces between the rather distant O atoms on opposite NO_2 groups are doubtless small, a considerable fraction of the molecules, even at low temperatures, will probably be oscillating widely about the equilibrium position, if not rotating freely. The oscillation motion will be strongly coupled to the other modes of vibration in such a way that these deviate from the frequencies and selection rules typical of the equilibrium position towards the frequencies and selection rules of the less symmetrical configurations taken up during the oscillation. For completely free rotation, the coupling will be so strong that the other vibrations will resemble exactly neither those of the plane nor the perpendicular models but will be intermediate between them. The long stretches of continuous absorption observed in certain regions may indicate some degree of free rotation.

DISSOCIATION OF N_2O_4

The energy of dissociation of N_2O_4 into 2NO_2 as given by equilibrium constants¹⁰ is 12.6 kcal., equivalent to 4440 cm^{-1} . N_2O_4 absorbs light of shorter wave-length than corresponds to its energy of dissociation in three strong, well-defined isolated bands, centers at 5197, 4778 and 4706 cm^{-1} .

¹⁵ Dennison, Rev. Mod. Phys. 3, 280 (1931).

¹⁶ Gerhard and Dennison, Phys. Rev. 43, 197 (1933).

We have analyzed these bands as combinations of vibrations within the NO₂ groups, corresponding to the bands $3\nu_r$ and $2\nu_r + \nu_r$ of single NO₂ and not of the vibration of the N—N bond (ν_{2rs}). As a result of this absorption the molecule is elevated to a quantized level of a potential surface above the convergence limit of the decomposition frequency (ν_{2rs}). The molecule may now either redistribute its energy into the N—N bond and decompose by a radiationless transfer through the col above the convergence limit or it may, more probably, lose this energy by collisions. The actual occurrence of discontinuous absorption is of interest from the standpoint of the old "radiation hypothesis" and as a verification of a phenomenon that has long been suspected to be possible.

Even if all the energy absorbed in this region

resulted in the decomposition of the molecule, the amount of infrared light needed to oppose measurably the thermal rate of formation is exceedingly high at ordinary temperatures (10^8 mols/sec. requiring 10^9 kcal./sec.). It may however be possible to decompose, at low temperatures, the white vitreous solid N₂O₄ into red NO₂ by infrared radiation between 1.92 and 2.25 μ .

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