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The Infrared Absorption Spectra of NO₂ and N₂O₄

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The infrared absorption spectrum of nitrogen peroxide has been investigated in the gaseous and liquid states, by 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. 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.

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 NO₂ and N₂O₄, it was decided to investigate the infrared absorption of nitrogen peroxide and extend the observations into the longer wave-length 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 NO₂ and N₂O₄.

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 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.

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 spectra for a more complete analysis.

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.

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 and Northrup galvanometer for secondary deflections, proved to be very useful in studying the

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[1] Daniels, J. Am. Chem. Soc. **47**, 2856 (1925).

[2] Warburg and Leithauser, Ann. d. Physik **28**, 313 (1909).

[3] Eva von Bahr, Ann. d. Physik **33**, 585 (1910).

[4] During the course of this investigation C. R. Bailey and A. B. D. Cassie have reported observations on this gas to 18μ and report several additional bands; Nature **131**, 239 (1933).
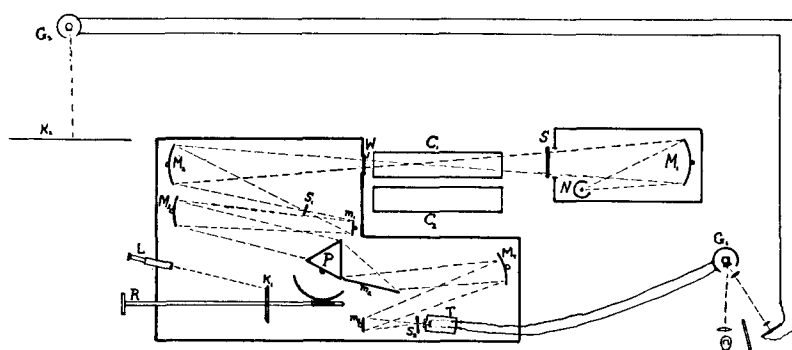
FIG. 1. Experimental arrangement.

longer wave-length 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 wave-length. 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 1.014μ and the CO_2 absorption band at 4.26μ. The indices of refraction for NaCl, taken from tables,[5] were plotted on a graph with wave-lengths through a range 0.5μ to 16μ. On a separate graph the angle of minimum deviation was plotted with the indices of refraction. The wave-length 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.

[5] Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 47.

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
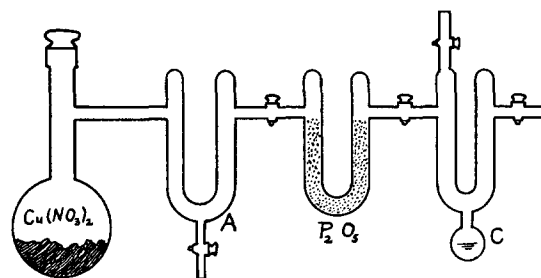

FIG. 2. Apparatus for preparing nitrogen peroxide.

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.

ABSORPTION SPECTRA OF NO_2 AND N_2O_4

The spectrum of nitrogen peroxide was mapped from 2μ to 16μ, by using absorption cells 10 cm in length with rocksalt windows and slit widths ranging from 0.08 mm to 0.5 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.

The observations on these bands were taken at a pressure of one atmosphere. The low
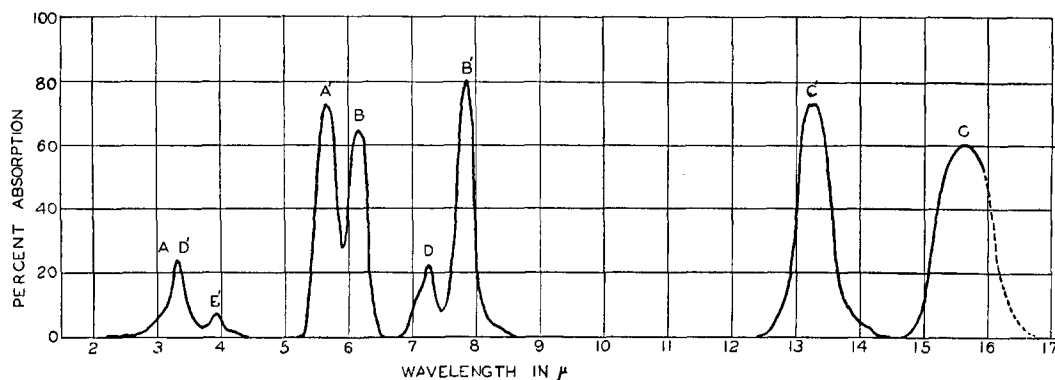
FIG. 3. Infrared absorption spectra of NO_2 and N_2O_4.

intensity of the band at 3.89μ did not permit accurate measurement of its wave-length.

It is known from chemistry that at ordinary temperatures 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 frequency of both NO_2 and N_2O_4, and that the absorption bands of both

gases in this region are nearly superimposed.

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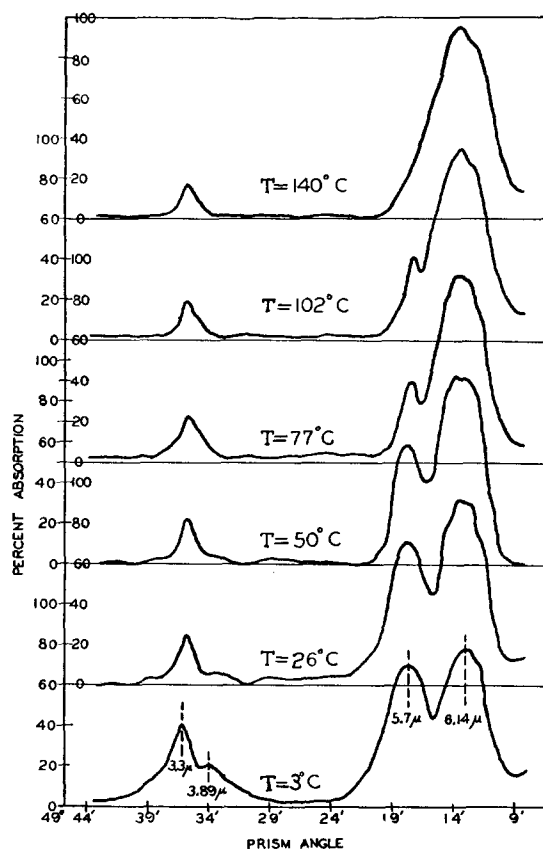
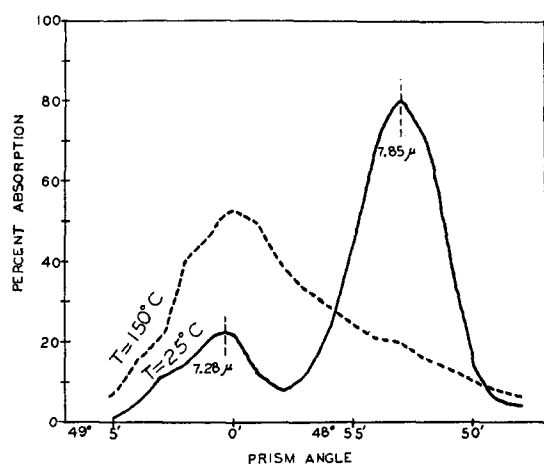FIG. 4. Infrared absorption of nitrogen peroxide at different temperatures in the region 2μ to 7μ.

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

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

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 $3.3\mu(D')$ 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, C. Bailey and Cassie give the wavelength of this band as 15.6μ.

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. After 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 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.

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

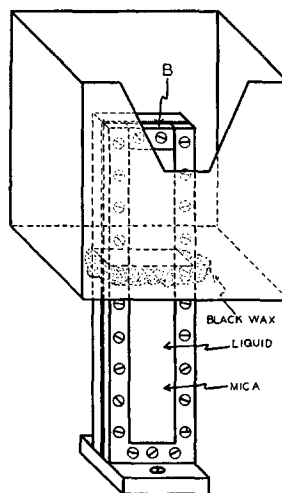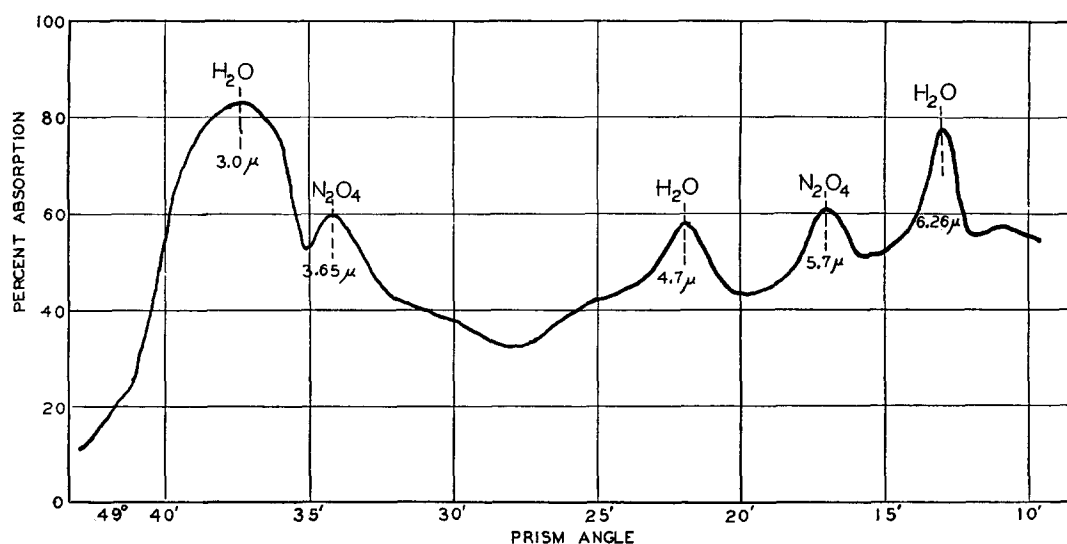FIG. 6. Cell used in studying liquid N_2O_4.

FIG. 7. Infrared absorption of liquid N_2O_4.

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 wave-length measurements of the 3.65μ band uncertain, and it is probable that its true wave-length 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, $\nu_1+\nu_3$, for NO_2 as shown in Table I. The observed value for this frequency is 3008 cm⁻¹.

The frequencies and wave-lengths of the absorption bands for NO_2 and N_2O_4 are shown in Table I. ν_1, ν_2, and ν_3 are assigned as the fundamental frequencies. The assignment in N_2O_4 is only tentative. It is probable that this molecule has more than three distinct funda-

mental frequencies. However, only three strong bands appear in the infrared absorption of this substance. The apparent simplicity of this spectrum makes it appear probable that the N_2O_4 molecule is symmetrical in structure.

TABLE I.

Band	Observed frequency in cm⁻¹	Calculated frequency in cm⁻¹	Combination	Wave-length in μ
NO₂				
A	3008	3001	$\nu_1+\nu_3$	3.30
B	1628		ν_3	6.14
C	641		ν_2	15.60
D	1373		ν_1	7.28
N₂O₄				
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