beam is accompanied by rapid disintegration of the luminescent material at the point of incidence of the beam.

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Form and Vibrational Frequencies of the NO₂ Molecule

BAILEY and Cassie¹ have recently presented data on the absorption of NO₂ — N₂O₄ gas mixtures in the region from 2.5μ to 16μ, from which they conclude that the NO₂ molecule is linear and symmetrical. As their conclusions and in some respects their data are in disagreement with results obtained recently in this Laboratory, and earlier results², we wish to present briefly the facts that lead us to conclude that the atoms in the NO₂ molecule are disposed as an obtuse angle triangle. Detailed reports will be published elsewhere.

The most cogent argument against a linear model is the complexity of the fine structure of the discrete absorption bands in the visible and ultra-violet. The isolated band of NO₂ at 2491 Å. clearly shows well-developed branches corresponding to rotations about two different axes of inertia, possible only if the molecule is non-linear in both the normal and excited states. We have examined the structure of the band under high resolution and find additional complexities associated with mutations about the third axis of inertia of magnitude indicating that the molecule is only slightly, but definitely, bent (apex half-angle > 55°) in the normal state. Weaker bands of practically identical structure occur at 751.1 and 1321.1 cm.⁻¹ on the long wave-length side of the 2491 Å. band. Quantitative measurements of the temperature coefficient of absorption make certain that these frequency differences belong to the normal state, and are presumably the fundamentals ν₂ and ν₁.

In the infra-red we have made measurements with a prism spectrometer from 1μ to 4μ using deep layers of gas under controlled conditions and find a number of bands which we can definitely ascribe to NO₂ or N₂O₄. Those found in NO₂ and the bands found earlier above 4μ can be accounted for as combinations and overtones of fundamentals 751, 1321, and 1621 cm.⁻¹. The last fundamental corresponds to the strongest band found at 6.17μ by Warburg and Leithauser and checked by Bailey and Cassie. Frequencies equal to the sum of observed frequencies are found, again excluding the possibility of the linear structure. However, it should be stated that we can also account for all our infra-red bands by using the two frequencies suggested by Cassie and Bailey and assuming an inactive frequency of 1010 cm.⁻¹. The infra-red data available do not permit a unique answer as to the structure.

Although lacking details of their experiments, we think it possible to reconcile Cassie and Bailey's data with our model, as follows. The band found by them at 13.4μ is in good agreement with our ν₂ = 751 cm.⁻¹, the deformation frequency; that at 6.17μ is the ν₃ fundamental. The fundamental

band corresponding to our ν₁ = 1321 cm.⁻¹, which should occur at 7.58μ, is missing. Inasmuch as the molecule is only slightly bent, we would expect this band to be the weakest fundamental; and it appears that the amount of gas in the absorbing layer was sufficient to bring out only the strongest bands, since they failed to report the strong 3.43μ band.

All the other bands, and possibly these also, may be ascribed to the N₂O₄ molecule, if the term molecule is not too definite to apply to what may be viewed as a more or less short-lived partnership of two NO₂ groups. In our infra-red work it is found that all the frequencies of NO₂ appear again in N₂O₄, indicating that the association bond is not strong enough to change appreciably the binding within the NO₂ groups. In addition, N₂O₄ has bands due to the extra degrees of vibrational freedom.

On our interpretation, calculation of the moment of inertia of NO₂ from the doublet separation of the 15.6μ band would have no significance; and such a calculation from the 6.17μ band must be regarded with caution, as a Q branch should be present. The intensity of the latter would however be small for a slightly bent molecule³ and might well be missed except by spectrometers of the highest resolution.

Further measurements in the infra-red are necessary to settle the difficulties mentioned above. However, it seems that the moments of inertia of NO₂ will be obtained most accurately from an analysis of the electronic band spectra.

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¹ NATURE, 131, 239, Feb. 18, 1933.

² Warburg and Leithauser, *Ann. Physik*, 28, 313; 1909. Daniels, *J. Amer. Chem. Soc.*, 47, 2856; 1925. Harris, *Proc. Nat. Acad. Sci.*, 14, 690; 1928. Herrmann, *Ann. Physik*, 15, 89; 1932.

³ Gerhard and Dennison, *Phys. Rev.*, 43, 197; 1933.

Sporangia containing Spermatozooids in Ferns

ALTHOUGH ferns have in a few instances shown some irregularities in the development of the haploid and diploid generation, such as appertain to apogamy

FIG. 1. Sporangia with (a) spermatozooids, (b) spores. × 1350.

and apospory, there has so far been little concrete evidence to homologise the sexual organs (or their content) with sporangia (or their spores) in ferns. The fact that spermatozooids have now been found in normal sporangia of *Scolopendrium vulgare* may