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Spectroscopic Evidence of the Dimerization of NO in the Gaseous State

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THE dimerization of nitric oxide in the condensed (liquid and solid) state already made obvious by magnetic measurements was definitively proved by Raman and infrared spectroscopy in a recent paper by Smith, Keller, and Johnston.[1]

On the other hand, it has been found by Vodar,[2] and confirmed by Bernstein and Herzberg,[3] that liquid NO exhibits a very strong continuous absorption throughout the ultraviolet; this absorption is very probably the result of N_2O_2 molecules.

Dimerization of NO in the gaseous state is substantiated by the data of Eucken and D'Or[4] on the second virial coefficient of NO at low temperatures.

If dimerization of NO occurs in the gaseous state, one expects to find a continuous absorption in the ultraviolet region of the spectrum.

Such an absorption has indeed been found[3] below 2600A with a path length of 30 meters of gaseous NO at a pressure of 700 mm of Hg; but unfortunately, a slight quantity of HNO_2 was present as an impurity, and it was not possible to decide if the continuous absorption was the result of HNO_2, of N_2O_3, or of N_2O_2 molecules.

It is to be expected that dimer molecules are more abundant at low temperatures; and, accordingly, we have taken the ultraviolet spectrum of gaseous nitric oxide between −180° and +20°C.

The absorption cell was a quartz tube one meter long, surrounded by a roughly thermally insulated jacket. Series of spectra were taken on the same plate in the following manner:

(1) The tube is filled, at room temperature, with pure gaseous NO at a pressure of 700 mm Hg; and a first spectrum is taken.

(2) Liquid air is poured into the jacket: the pressure decreases rapidly, owing to the condensation of NO on the walls of the tube. A second spectrum is taken when the pressure has reached a value of 1.5–2 mm Hg.

(3) The temperature is allowed to rise gently, a series of spectra being taken during this time. These spectra are characterized by the following important features:

(a) The rising of temperature is first accompanied by the development of a more and more intense continuous absorption, which is overlapping the bands of NO. The most intense absorption is found in the spectra taken at a temperature very close to the boiling point of NO. *These spectra correspond to the lowest temperature consistent with the maximum number of molecules; the fact that they just show the most intense absorption is very significant.*

(b) A further rise of temperature above the boiling point of NO is accompanied by the regress of the continuous absorption.

The last spectrum was taken after returning to room temperature: it does not differ in any way from the first spectrum; consequently, *the substance responsible for the continuous absorption appears at lower temperatures and disappears at higher temperatures by a completely reversible process.*

(c) The spectra taken in a convenient range of temperatures and pressures exhibit, between 2360 and 2320A, a very weak system of diffuse bands. Maxima of absorption were found at 2353, 2345, 2338, and 2330A (42.486, 42.631, 42.758, 42.905 cm^{-1}).

These measurements give only rough values, owing to the weakness and diffuseness of the bands, but they suggest a frequency interval of the order of 140 cm^{-1}. *This low value is to be compared with the frequency 167 cm^{-1} found in the Raman spectrum of liquid* NO, *and which is undoubtedly a fundamental frequency of the dimer* N_2O_2.

The interpretation of these results by the existence of dimer molecules N_2O_2 in gaseous nitric oxide is almost obvious. Further experiments with a more refined apparatus are now in course with the purpose of measuring the bands with accuracy.

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[1] Smith, Keller, and Johnston, J. Chem. Phys. 19, 189–192 (1951).

[2] B. Vodar, Compt. rend. 204, 1467 (1937).

[3] H. J. Bernstein and J. H. Herzberg, J. Chem. Phys. 15, 77 (1947).

[4] Eucken and D'Or, Nachr. Ges. Wiss. Göttingen, F. III (17), 107 (1932).

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