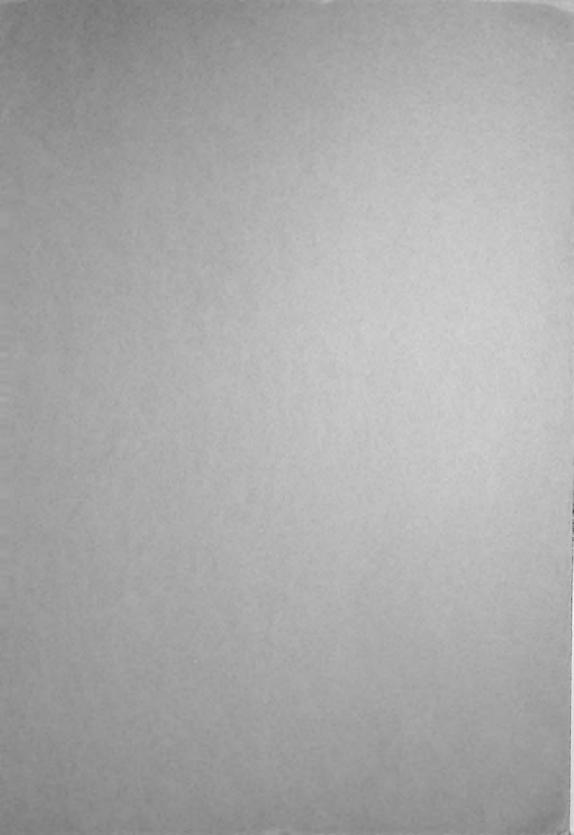
Spectroscopic Evidence of the Dimerization of NO in the Gaseous State

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HE 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 N2O2 molecules.

Dimerization of NO in the gaseous state is substantiated by the data of Eucken and D'Or4 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 found³ 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 HNO2 was present as an impurity, and it was not possible to decide if the continuous absorption was the result of HNO2, of N2O3, or of N2O2 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 $+20^{\circ}$ 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 N2O2.

The interpretation of these results by the existence of dimer molecules N2O2 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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