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Ultraviolet Absorption of Mixtures of NO, NO₂ and H₂O

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In considerable amounts of NO containing small amounts of NO₂ a continuous absorption occurs in the ultraviolet, obscuring both the absorption of NO and that portion of the absorption of NO₂ which lies below 2500Å. The behavior of this absorption with respect to temperature and the partial pressures of the constituents is rather convincing evidence that it is due to N₂O₃. When very small amounts of water are also present a group of bands occurs in the near ultraviolet, lying in the same region but

not resembling the longer wave-length NO₂ absorption. These bands appear diffuse under low dispersion but possess an ordered arrangement. With increase of temperature the intensity of the bands decreases rapidly. They begin in the vicinity of 3850Å, extending to shorter wave-lengths. The first members are broader and more diffuse than those that follow, indicating a predissociation process in the carrier, which is probably HONO.

WHEN the absorption spectrum of pure nitric oxide is photographed in moderate path lengths at atmospheric pressure and room temperature with quartz and ordinary unsensitized plates, the entire spectrum consists of the 0-0 band of the γ system with perhaps the 0-1 band also showing at the extreme short wave-length limit. If a very small amount of oxygen or of nitrogen dioxide be present, however, a continuous absorption overlies this region of the NO bands, which is due to the molecule N₂O₃. If, in addition, a very small amount of water vapor be present, a series of bands appears in the region 4000-3000Å which are not characteristic of the NO₂ spectrum, nor, of course, of that of NO. The authors have earlier reported¹ discovering these absorptions during work on the optical dissociation of N₂O, and at that time erroneously attributed the bands also to the carrier N₂O₃. The presence of water vapor as well as both the other constituents is necessary for the production of

the bands. A probable carrier of the bands would seem to be the molecule HONO, though a polymer of this molecule would also be a possibility. In this paper they will be referred to as due to HONO, or, as is more often written, HNO₂.

The absorption bands are shown as the two lower portions of Fig. 1, with the absorption of NO₂ above for comparison. Though the positions of such diffuse bands can hardly be given wave-length values with useful accuracy, these bands nevertheless suggest that they comprise two progressions, as is diagrammatically illustrated below the absorption in the figure. The bands set in remarkably close to the position of the first predissociation process in NO₂. The first bands are very diffuse, sharpening noticeably as they proceed to shorter wave-lengths.

If these bands are due to HONO, or a polymer of this, they should show a dependence upon the pressures of the three constituents NO, NO₂ and H₂O, and probably upon the temperature of the mixture, depending upon the magnitude of the

¹ Melvin and Wulf, *Phys. Rev.* **38**, 2294 (1931).

heat of dissociation of HONO. The continuous absorption due to N_2O_3 should similarly show a dependence upon the pressures of NO and NO_2 , and also upon the temperature of the mixture, this latter following from the fact that the heat of dissociation of N_2O_3 into NO and NO_2 has been found to be about 10,300 calories.² All of these conditions are fulfilled.

In Fig. 2 the upper picture shows these absorptions at three different partial pressures of NO_2 in a 40-cm path length and constant partial pressure of H_2O and NO, the first strip being the light source through the empty cell, the next lower being taken with H_2O at a pressure of 16 mm Hg and NO at roughly 544 mm Hg (this amount of NO is so great that the $v''=1 \rightarrow v'=0$ band shows in absorption at the short wave-length end, even at room temperature). The last three strips show the absorption for approximately 0.5 mm, 1.5 mm and 4.5 mm Hg pressure, respectively, of added NO_2 . The lower picture in Fig. 2 is similar, showing the light source through the empty cell, through the cell containing 7.4 mm of NO_2 , and thirdly with 5.2 mm of H_2O added, while in the three lower strips NO was added to the cell in three increasing amounts, roughly 35 mm, 215 mm, and 760 mm Hg, respectively.

In Fig. 3 the upper picture shows in a similar way the influence of water vapor, the first strip being the source through the empty cell, the second with the cell containing approximately 7.4 mm of NO_2 and the third with 470 mm of added NO. The three following strips were taken after the addition of water vapor in amounts roughly 0.9 mm, 6.1 mm, and an amount which would have given 41.5 mm Hg had not some undoubtedly condensed out on the walls. In the lower picture of Fig. 3 these absorptions are shown at three different temperatures, the NO_2 pressure being 1.5 mm Hg, the NO pressure 380 mm Hg, and the H_2O pressure 20 mm Hg.

It should be stated that the introduction of the gases into the absorption cell always involved condensing out in a small U-tube, contained in the circulating system which was in series with the absorption cell. This means that

the solid and liquid phases were always present, for a short time at least, prior to the above exposures. An all-glass magnetic piston-type pump effected the circulation and resultant mixing. The various amounts of gas added to the cell are given above as pressures they would have exerted had they been alone in the absorption tube system.

There is a further observation which lends weight to the point of view that the bands are due to HNO_2 . If, to a cell containing a small amount of NO_2 , water vapor be added in excess of saturation until a small amount of liquid water must exist as a film on the walls, the NO_2 may be reduced to a value so low that it cannot be seen. This is probably due to the formation of HNO_3 and NO, the NO making its appearance in absorption. If now NO be added in excess the HNO_2 bands become plain, the NO effecting an increase in the concentration of the HNO_2 which may be many fold, depending upon the degree of dissociation of the HNO_2 prior to the addition.

Certain of the bands give the impression of being related to the NO_2 absorption, because of the close correspondence of their positions with some of the NO_2 bands. However, in the case of such diffuse bands and such relatively low dispersion this may well be fortuitous.³

DISCUSSION

At least two suggestions might be made as to the significance of the two groups of bands. They might be thought of as transitions in but one degree of oscillational freedom for which $v''=0$ and $v''=1$. This does not seem probable, however, because the relative intensities of the two progressions to be expected on such a basis do not seem to exist. With increasing temperature the intensity of both progressions decreases rapidly as would be expected owing to the decrease in the concentration of the HONO through thermal dissociation. There is, however, no noticeable tendency for the weaker progres-

³ If this were a real correspondence one might ascribe the bands to a selective enhancement of certain of the NO_2 bands by the mutual action of NO and H_2O . It seems, however, that such an explanation would not differ greatly from attributing the bands to HNO_2 or a polymer thereof.

² Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

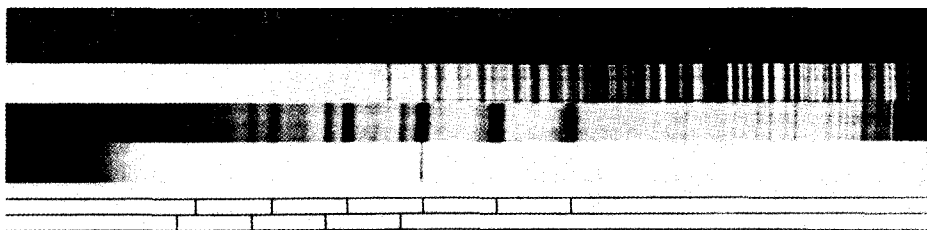


FIG. 1. Absorption bands occurring in mixtures of NO, NO₂ and H₂O, probably due to HNO₂. The absorption of NO₂ is shown above.



FIG. 2A. The effect of increasing nitrogen dioxide, showing at left the continuous absorption of N₂O₃, and at the right the absorption bands of HNO₂.

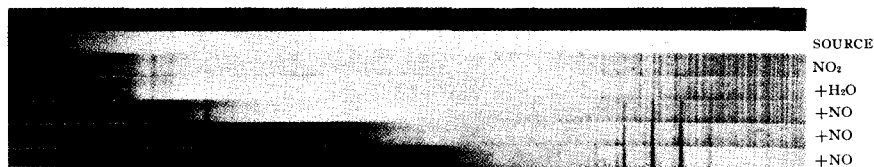


FIG. 2B. Similarly, the effect of nitric oxide.

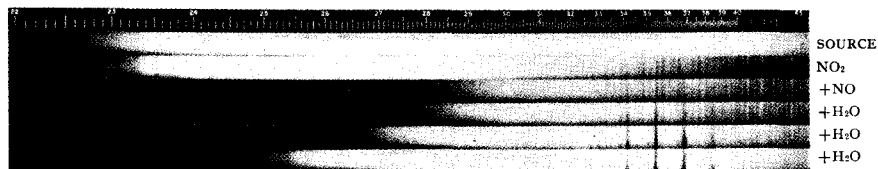


FIG. 3A. The effect of increasing water, showing the decrease of the N₂O₃ absorption, and the increase of that of HNO₂.



FIG. 3B. Effect of increasing temperature, showing the disappearance of N₂O₃ and HNO₂, and the appearance of NO and NO₂.

sion of the bands to decrease less rapidly than the other progression, which on the interpretation mentioned at the head of this paragraph would be brought about due to the partial off-setting of the decrease in the concentration of the carrier by the increase in the Boltzmann quota of molecules in the vibrational level $v''=1$. If the bands did represent two progressions for which $v''=0$ and $v''=1$, then a minimum value for the initial separation of the levels in this fundamental frequency would be roughly 750 cm^{-1} . Now one may compare the change in the ratio of the numbers of molecules in the zeroth and first vibrational states at 298°K and 473°K with the relative intensity of the bands at these two temperatures. Assuming equal statistical weights, this frequency separation leads to a ratio of populations in the two states at room temperature of roughly 0.027, while at the higher temperature it is about 0.103. This change in relative intensity of only 4-fold might, however, be present in such a mixture of absorptions without being noticeable. However, the ratio of intensities to be expected at room temperature, namely, about 40-fold, also hardly seems to be substantiated in fact, though in the absence of quantitative photometric measurements it cannot be ruled out. It is perhaps doubtful if even the latter would be very conclusive in this mixture of absorptions, and with the NO_2 absorption itself changing somewhat with the temperature.

TABLE I. Absorption bands of HNO_2 .

WAVE-LENGTH (Å)	WAVE NUMBER (cm^{-1})	DIFFERENCES (cm^{-1})
3843	26014	
3681	27159	
3539	28248	
3510	28482	234
3416	29266	784
3388	29507	241
3307	30230	723
3278	30498	268
3204	31202	704
3177	31467	265

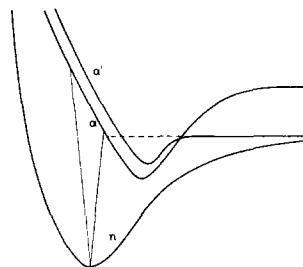


FIG. 4. Diagrammatic potential energy curves.

An alternative hypothesis seems in better accord with the observations, namely, that the transitions all originate from the same normal level and go to several levels in one mode of oscillation in the excited state and to two levels in a second mode of oscillation in the excited state, thus yielding the two partial progressions. From Fig. 1 it can be seen that, on the basis of the first hypothesis, there is the opportunity to obtain three estimates of the separation $v''=1$ to $v''=0$, while on the basis of the second hypothesis there is the opportunity to obtain four estimates of the separation $v_2'=1$ to $v_2'=0$. Table I gives the data for these bands and these two sets of differences. In this comparison lies also a slight indication in favor of the second hypothesis, since in the case of the first estimate, instead of being constant the three observed values decrease progressively, being 784 cm^{-1} , 723 cm^{-1} , and 704 cm^{-1} , respectively, while in the second case the four observed differences are 234 cm^{-1} , 241 cm^{-1} , 268 cm^{-1} and 265 cm^{-1} . The failure of the former to show constancy argues against the first hypothesis, and everything considered the second seems the more probable. The authors obtained similar results in a study of the effect of temperature upon the absorption bands of ozone.⁴ In this case the bands are very numerous, and several levels of at least two modes of vibration in the excited state are evident. In spite of this no bands were observed which came from levels of the normal state appreciably higher than the lowest. Since this work, Chalonge and Lefebvre,⁵ working with

⁴ Wulf and Melvin, *Phys. Rev.* **38**, 330 (1931).

⁵ Chalonge and Lefebvre, *Comptes rendus* **197**, 444 (1933); *ibid.* **199**, 456 (1934).

very large effective paths of ozone, have found bands at longer wave-lengths which come from higher vibrational levels in the normal state.

The beginning of the HONO bands so nearly at the point of the first predissociation of NO₂ suggests that there may be a connection between these two phenomena. The exceptional diffuseness of the first bands indicates that at about this energy there exist discrete vibrational states of an electronic level in HONO from which there is a high probability of transition into another electronic level in the molecule, in which, for this energy, the molecule is dissociated, whereas for vibrational states higher than these the probability of transition into this second level grows less. Fig. 4 shows diagrammatically one arrangement of levels in the molecule that could lead to such circumstances,⁶ pictured as if but one of the fundamental frequencies of this polyatomic molecule were excited, that is, as if one were dealing with a diatomic molecule.

Franck, Sponer and Teller⁷ have discussed predissociation in polyatomic molecules and have explained important differences from the behavior of diatomic molecules that may in general arise. Gradual setting-in of predissociation is one of the important differences. In diatomic molecules it is very improbable, to be expected only where the potential curve of the upper level and the perturbing level intersect in an extremely acute angle. In polyatomic molecules, however, where the relative positions of the atoms are determined by three or more parameters, factors arise in the complicated motion of oscillation which can lead to a gradual setting-in of predissociation, and here it is frequently encountered. But the present case, in contrast, shows a gradual decrease of diffuseness as one passes to higher v' levels. This behavior is in general less to be expected in polyatomic molecules. It becomes possible, however, if the excitation is chiefly in one degree of freedom, and this, indeed, seems to be true in the present case.

The experimental observation that the bands, starting very diffuse, become sharper with in-

creasing frequency seems to be quite certain. It is to be noted that both the increasing dispersion and, for the first few bands also the increasing intensity, act to minimize the appearance of this effect; it is, however, quite apparent in spite of these. This appears to be one of the simplest and most apparent cases of this phenomenon. How far this sharpening of the bands, after the first few, is continued, cannot be said, for they rapidly become faint and are lost in the continuous absorption of N₂O₃.

There are difficulties in the way of obtaining the bands more intensely. Temperature change is of little help, an increase decomposing the HONO, and a decrease reducing its concentration through the reversion of NO₂ to N₂O₄ and the decrease in the saturation pressure of water. Increasing the absolute amount of NO₂ obscures the region by its own absorption. The factor which promises a decidedly favorable change is the pressure of NO. If this could be raised considerably above one atmosphere, an appreciable gain in the concentration of HONO molecules would be expected.

It would be pertinent to raise the question as to the N₂O₃ content of "pure NO₂," for in a mixture of as pure NO₂ ⇌ N₂O₄ as one can prepare there exists the equilibrium 2NO₂ = N₂O₃ + $\frac{1}{2}$ O₂. Using the free energy value given by Verhoek and Daniels² for the reaction NO₂ + NO = N₂O₃, $\Delta F_{298^\circ} = +441$ calories, and that given in the *International Critical Tables*⁸ for the reaction NO₂ = NO + $\frac{1}{2}$ O₂, $\Delta F_{298^\circ} = +8374$ calories, one immediately sees that at room temperature this amount of N₂O₃ will be very small. For NO₂ pressures of a few millimeters the partial pressure of N₂O₃ is of the order of 10⁻⁵ that of NO₂.

It is interesting that, in the path lengths we have used, the absorption in the red or orange that leads to the blue color of liquid N₂O₃ has not yet been observed. It may be that longer paths will show it. It may also be that this absorption is due to a higher association product such as N₄O₆, appearing with appreciable strengths only at high densities as in the liquid.

⁶ Franck and Sponer, Nachr. d. Gesell. d. Wiss. zu Göttingen, p. 241 (1928).

⁷ Franck, Sponer and Teller, Zeits. f. physik. Chemie B18, 88 (1932).

⁸ *International Critical Tables*, Vol. 7, p. 239.