AIP | The Journal of Chemical Physics

Predissociations in Nitric Oxide

P. J. Flory and H. L. Johnston

Citation: The Journal of Chemical Physics **14**, 212 (1946); doi: 10.1063/1.1724119
View online: http://dx.doi.org/10.1063/1.1724119
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/14/3?ver=pdfcov
Published by the AIP Publishing

Predissociations in Nitric Oxide

P. J. FLORY
Research Department, The Goodyear Tire and Rubber Company, Akron, Ohio
AND H. L. JOHNSTON
Department of Chemistry, The Ohio State University, Columbus, Ohio

(Received January 25, 1946)

GAYDON,[1–3] in a series of recent publications, has argued for a heat of dissociation of nitrogen of 9.764 ev, in place of the previously accepted value of 7.384 ev.[4] The heats of dissociation of nitric oxide calculated from these two values of D_{N_2}, in combination with thermochemical data and $D_{O_2}=5.09$ ev, are 6.49 and 5.29 ev, respectively. An obvious objection to the higher value of D_{NO}, and hence to Gaydon's D_{N_2} as well, is the previous suggestion of Kaplan[5] that the absence of β-bands in emission from vibrational level in the upper electronic state ($^2\pi$) beyond $v'=4$ is due to predissociation. This level corresponds to 6.12 ev, which is below the dissociation energy required by the higher value for D_{N_2}. Gaydon,[3] however, has now succeeded in locating emission bands of the β-system arising from upper levels for which $v'=5$ and 6, thus refuting previous *spectroscopic* evidence for predissociation in the β-system and thereby eliminating an objection to the higher dissociation energies.

Gaydon does not confine his renunciation of previous conclusions concerning predissociations of nitric oxide to those pertaining to the β-system. He apparently regards all evidence for predissociation from any of the excited levels of nitric oxide as worthless, dismissing it indiscriminantly as the product of "wishful thinking."

An investigation of the photo-decomposition of nitric oxide carried out by the present author[6] some time ago led them to the conclusion that at low pressures, using wave-lengths from 1800 to 2000A, the primary process is one of predissociation; under our experimental conditions the $\delta(1,0)$-band appeared to be principally responsible for the absorption causing decomposition. Gaydon[3] disposes of this work with the following remarks: "With the new knowledge that $B^2\pi$ [upper state of the β system] is not predissociated below $v=6$, and that state D [upper state of the ϵ bands] is of type $^2\Sigma^+$, and is not predissociated below $v=2$, it becomes clear that their [Flory and Johnston's] explanation of the photodissociation is certainly incorrect in detail and may be altogether wide of the mark. From inspection of the potential curves it would clearly be very difficult to imagine any repulsive curve which could predissociate $C^2\Sigma$ [upper state for the δ bands] below $v=1$ without also causing predissociation in $D^2\Sigma^+$ (the curve for which lies very close indeed to that for C) and $B^2\pi$. It may be noted that Flory and Johnston's observations are at variance with those of Macdonald (1928)."

Our measurements show conclusively that over the pressure range investigated, 0.02 to 7 mm, the rate of decomposition caused by the full radiation emitted by a low pressure mercury arc in quartz is directly proportional to the amount of Beer's law absorption, the rate being otherwise independent of pressure. The mere fact that rapid photo-decomposition occurs at these low pressures, where the mean lifetime with respect to collision far exceeds the life with respect to fluoresence, is strong indication of a monomolecular decomposition; the observed dependence of the rate on pressure firmly establishes this conclusion. The decomposition produced by the mercury arc was shown to be almost entirely due to radiation between 1800 and 1900A, the lower limit being imposed by absorption by quartz and air. Most of the decomposition appeared to be produced by wavelengths below 1850A. In this region the nitric oxide absorption spectrum is banded; hence, the

---

[1] A. G. Gaydon and W. G. Penney, Nature **150**, 406 (1943); A. G. Gaydon, *ibid.* **153**, 407 (1944).
[2] A. G. Gaydon, Proc. Phys. Soc. (London) **56**, 95 (1944).
[3] A. G. Gaydon, Proc. Phys. Soc. (London) **56**, 160 (1944).
[4] G. Herzberg and H. Sponer, Zeits. f. physik. Chemie **B26**, 1 (1934). See G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1941), pp. 477–9.
[5] J. Kaplan, Phys. Rev. **37**, 1406 (1931).
[6] P. J. Flory and H. L. Johnston, J. Am. Chem. Soc. **57**, 2641 (1935).

monomolecular dissociation must be a predissociation.

It was shown further that in this spectral region only the $\delta(1,0)$-band at 1830A is of sufficient intensity to account for the observed dependence of rate on nitric oxide pressure. (The spectrum of the mercury arc was rich in continuous radiation extending from the 1849A-resonance line to well below 1830A, in which region the weaker 1832A-line was included.) Hence, we concluded that predissociation occurred from the $v=1$ level of the $^2\Sigma$-state (upper state of the δ-bands). In conformity with this conclusion, no emission bands are known which arise from this or higher levels of the same electronic state, although intense absorption bands are known which involve these levels. The excitation energy associated with absorption by the $\delta(1,0)$-band is 6.77 ev, which is larger than either D_{NO} value.

Certain of our results obtained using filtered radiation from various spark sources showed that wave-lengths above 1900A, but probably below about 2000A, produced appreciable decomposition at nitric oxide pressures around 0.1 mm. They were considerably less effective than shorter wave-lengths, however; this might be expected merely from the markedly lower intensity of absorption in this region. We suggested at that time that β-band predissociation probably was responsible for decomposition by these longer wave-lengths, an interpretation which would seem to be incompatible with Gaydon's observation of emission bands from $^2\pi$, $v=5$ and 6 levels. However, the observation of emission bands does not necessarily preclude a weak predissociation which may occur only to the extent that the emission intensity is reduced, but not eliminated entirely.

Regardless of which bands are responsible for the effect, it is significant that wave-lengths above 1900A effect decomposition. It seems very doubtful to us that the observed effects here were confined to wave-lengths between this lower limit and 1910A, the wave-length corresponding to Gaydon's $D_{\mathrm{NO}}=6.49$ ev. It would be extremely difficult to account for the decomposition at the low pressure employed by assuming a bimolecular process. Hence, these admittedly rather limited observations on the decomposition of nitric oxide by wave-lengths above 1900A cast doubt on the high value of D_{NO} proposed by Gaydon.

In conclusion we should like to point out that our results show conclusively that predissociation occurs when nitric oxide is irradiated with wave-lengths around 1800 to 1850A. The $\delta(1,0)$-band almost certainly is responsible for the overwhelming portion of this decomposition. Admittedly there may be some difficulty in postulating a repulsive state which dissociated $C^2\Sigma$, $v'=1$, while molecules in the neighboring $D^2\Sigma^+$, $v'=1$ (upper state for the ϵ-bonds) emit radiation; the latter apparently does not undergo predissociation at all, or does so with greater difficulty. Nevertheless, we wish to emphasize that this apparent incongruity does not justify dismissal of the photochemical results.

It should also be mentioned, contrary to Gaydon's statement, that our results do not conflict with those of Macdonald. His work was conducted at higher pressures, and, as we pointed out, a different spectral region probably was involved in his experiments.