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Predissociation of the Oxygen Molecule*

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In the emission spectrum of the oxygen molecule no bands in the Runge system, ${}^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$, having $v' > 2$ have ever been observed. The absence of these emission bands as well as evidence of broadened rotation lines in the $v' > 2$ absorption bands suggests that in the ${}^3\Sigma_u^-$ state vibration levels above the second undergo predissociation. Rassetti's observations of the fluorescence spectrum of oxygen as well as recent photochemical results support this conclusion. Although it cannot be said that any one of these lines of evidence provides rigorous proof that the oxygen

molecule predissociates, collectively they present a convincing argument for the occurrence of predissociation. Radiationless transition from the ${}^3\Sigma_u^-$ state is doubtless to the ${}^3\Pi_u$ state formed from normal atoms. On the basis of the present interpretation the initial process in the photochemical reactions of oxygen caused by light in the region of Schumann-Runge band absorption is the formation of normal 3P atoms as a result of the predissociation, rather than the reaction of an optically excited molecule with a normal molecule as heretofore has been supposed.

INTRODUCTION

IN studies of the photochemical reactions of oxygen, other than those carried out at high pressures, it has been customary to distinguish between the effects of light absorption in two different spectral regions. The first region is that of the Schumann-Runge absorption bands which extend from about 2000Å down to their convergence limit at 1751Å. The second region lies below the convergence limit and consists of strong continuous absorption. Differences in the photochemical effects of radiations falling in these two regions have been attributed to the difference in the reactivity of an optically excited oxygen molecule produced by band absorption and the reactivity of the oxygen atoms resulting from the continuous absorption. For instance, Smith and Kistiakowsky¹ have found that the relative yields of ozone and hydrogen peroxide in hydrogen-oxygen mixtures differ when the 1854–1862Å lines are used and when the 1719–1725Å lines of aluminum are used. It is the purpose of this paper to show, on the basis of data already in the literature, that predissociation occurs in the region of band absorption. The predissociation results in the production of two unexcited 3P oxygen atoms whereas the continuous absorption produces one 3P and one excited 1D atom. Consequently, differences in the photochemical effects of light in the

two spectral regions are due to the difference in the states of the atomic dissociation products.

THE OXYGEN SPECTRUM AND PREDISSOCIATION

The Schumann-Runge band system, ${}^3\Sigma_u^- \leftrightarrow {}^3\Sigma_g^-$, is responsible for the only absorption of oxygen in the visible and ultraviolet regions down to about 1000Å, except for weak absorption due to forbidden transitions which is only observed with large optical densities. The (0, 0) band at 2026Å is extremely weak. Proceeding to shorter wave-lengths the intensity of the successive absorption bands increases rapidly. The bands converge at 1751Å, and the continuous absorption below this point continues to increase in intensity until a maximum is reached at about 1450Å.²

Runge³ photographed the same system of bands in emission in the second and third orders from a 6.5-meter grating. His source was a high potential d.c. arc operated in a quartz tube through which oxygen was streaming. Lochte-Holtgreven and Dieke,⁴ using Runge's plates, analyzed the rotation structure of the bands indicated in Fig. 1. In the region from 3050 to 4450Å they classified *all lines*, except weak and sporadically occurring ones, into these nineteen bands. Nine of the bands belong to the $v' = 0$ progression, five to the $v' = 1$, five to the $v' = 2$, and none to higher progressions. No evidence of emission from excited levels having $v' > 2$ was found. On

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¹ Smith and Kistiakowsky, *J. Am. Chem. Soc.* **57**, 835 (1935).

² Ladenburg and Van Voorhis, *Phys. Rev.* **43**, 315 (1933).

³ Runge, *Physica* **1**, 254 (1921).

⁴ Lochte-Holtgreven and Dieke, *Ann. d. Physik* **3**, 937 (1929).

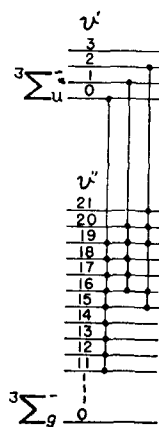


FIG. 1.

the basis of the Franck-Condon principle a number of such bands should have been observed in this spectral region. For example, the (3,15), (3,16), (3,20), (3,21), and (3,22) bands, all of which would fall within the spectral region investigated, lie close to the Condon curve of maximum intensities. Although the failure to observe these bands may have been the result of some experimental peculiarity, it appears to be much more probable that they are inherently absent, or greatly reduced in intensity, in the emission spectrum of oxygen. If this is the case, the absence of $v' > 2$ progressions must be due to some process which destroys or deactivates molecules in vibration levels above $v' = 2$ before they can emit radiation.

In a number of cases a breaking off in the emission spectrum such as occurs here has been associated with predissociation of the levels from which emission is absent. That is, if the probability of predissociation is much greater than the probability of emission (fluorescence), then the emission will be so weak as to escape observation. In fact, this has been used frequently as a criterion for predissociation. Predissociation of the $^3\Sigma_u^-$ state of oxygen for $v' > 2$ levels would plausibly explain the absence of emission from such levels. In what follows this explanation will be shown to be in agreement with other lines of evidence.

Predissociation is most commonly recognized by the diffuse rotation lines of the absorption bands. In many instances rotation structure is entirely lost. The degree of broadening in any case is simply dependent upon the mean life of

the excited state prior to predissociation. Recently Curry and Herzberg⁵ have carefully analyzed the (1,0), (2,0), (3,0), (4,0), (5,0), (4,1), (5,1), (6,1), and (7,1) absorption bands of oxygen obtained with air in their grating spectrograph. Although they measured the rotation lines at a dispersion of 1.7 Å per mm, they do not mention predissociation. However, they point out that their most accurate measurements were made on the (2,0) band. Here the error in their measurements was about $\pm 0.2 \text{ cm}^{-1}$, whereas the errors in the seven bands of higher v' ran as high as $\pm 0.8 \text{ cm}^{-1}$. (Curry and Herzberg attribute the error to the characteristics of the line, i.e., intensity, overlapping, and breadth). Also, in the photograph which they publish the lines in the (2,0) band appear to be sharper than those in the neighboring (5,1) band, and in the (3,0), (6,1), and (4,0) bands. These observations, though in themselves inclusive, are indicative of an actual line broadening in $v' > 2$ bands.

The absence of fluorescence from levels which predissociate has frequently been used as a sensitive test for predissociation. Rasetti⁶ photographed an extremely weak fluorescence spectrum when he irradiated oxygen at atmospheric pressure with an intense mercury arc. The strong mercury 1849 line excited the oxygen molecules into the $^3\Sigma_u^-$, $v' = 8$, $J = 12$ and $J = 8$ levels. In the fluorescence spectrum eighteen lines, all from these two upper levels, were found. In order to photograph the fluorescence it was necessary to run the exposures from fifty to eighty hours. Such a weak emission must mean that only a very few of the optically excited molecules dispose of their energy by fluorescing, a conclusion in agreement with the characteristics of the oxygen emission and absorption spectra discussed above.

Rasetti presumed that the low intensity of fluorescence was due to quenching of the excited molecules by collisions with other molecules. He was surprised, therefore, to find that on lowering the pressure to 8 mm so as to reduce the number of quenching collisions he could no longer obtain the fluorescence spectrum at all.

⁵ Curry and Herzberg, *Ann. d. Physik* **19**, 800 (1934). Recently Knauss and Ballard (*Phys. Rev.* **48**, 796 (1935)), have reported measurements and analyses of the $v' = 7$ to 15 absorption bands in the $v'' = 0$ progression. Their dispersion was not sufficiently high to show predissociation broadening.

⁶ Rasetti, *Proc. Nat. Acad. Sci.* **15**, 411 (1929).

It was Rasetti's expectation, presumably, that inasmuch as the absorption was almost complete at atmospheric pressure, a hundred-fold decrease in pressure would reduce the amount of light absorbed much less than it would reduce the collision rate, and the net result would be an increase in fluorescence intensity. The failure to observe any fluorescence at the lower pressure is not surprising if, alternatively, the destruction of the excited molecules is not dependent upon collisions, in other words, if it is due to predissociation. Thus, predissociation of oxygen in the ${}^3\Sigma_u^-$ state not only accounts for the low intensity of the fluorescence observed by Rasetti, but it also explains his failure to observe fluorescence at the lower pressure.

PHOTOCHEMICAL EVIDENCE OF PREDISSOCIATION

Neujmin and Popov⁷ in conjunction with their investigation of the photochemical reaction of oxygen and hydrogen observed photochemical effects produced in oxygen alone at pressures of about 0.1 mm. When the oxygen was subjected to light from a hydrogen discharge tube in the region of its continuous absorption from 1751Å (the convergence limit of the Runge bands) down to about 1300Å, the pressure decreased due to the reaction of the photochemically produced atomic oxygen with the picein or shellac used to attach the cell windows. The atomic oxygen was also shown to react with impurities on the cell walls unless these had been carefully cleaned by baking at red heat under vacuum. These experiments suggest that such a decrease in pressure due to reaction with impurities might serve as a criterion for the presence of oxygen atoms at low pressures.

When Neujmin and Popov, by interposing air in the light path, limited the exciting radiation to that lying above 1751Å where only band absorption can occur, no pressure decrease similar to that mentioned above was observed. They considered that only excited molecules resulted from the band absorption. Since at 0.1 mm the time between collisions (about 10^{-6} sec.) is much greater than the life of an excited molecule with respect to fluorescence (10^{-9} to 10^{-8} sec.) they attributed their failure to observe evidence of

reaction to the predominating disposal of excitation energy by fluorescence. These results might be interpreted to demonstrate the absence of oxygen atoms when oxygen is irradiated with light in this region. This interpretation is, of course, incompatible with the occurrence of predissociation.

In connection with their investigation of the photochemical decomposition of nitric oxide, Flory and Johnston⁸ have obtained results which show that such an interpretation must be incorrect. In view of the important bearing of these results on the present problem it will be well to consider them in detail here. The reaction system, essentially the same as that used by Neujmin and Popov, was entirely of Pyrex and quartz and pressures were measured on a McLeod gauge. Although the reaction system was frequently "flamed out" under vacuum, it was never baked out intensively as Neujmin and Popov have shown to be necessary in order to eliminate the reaction of atomic oxygen with impurities. The 1775, 1832, and 1849 lines and some continuous radiation in the region of oxygen band absorption were present in the mercury arc source of illumination. The absence of light below the convergence limit was assured by the presence of about a centimeter of air between the arc and the cell window. The pressure decreased steadily from 0.1280 to 0.0963 mm in $7\frac{1}{2}$ hours and remained constant after discontinuing the illumination.

The results of this single experiment are substantiated quantitatively by the results of a number of others in which nitric oxide was first completely decomposed into nitrogen and oxygen. A subsequent pressure decrease, obviously due to a photo-reaction of the oxygen since nitrogen is transparent in this spectral region, was found to occur on further illumination. The fractional decrease per hour in the pressure of oxygen was about the same as that observed in the experiment with pure oxygen under the same conditions of illumination.

A bimolecular collision of an optically excited molecule with a normal molecule, as Neujmin and Popov point out, is much less probable at pressures around 0.1 mm than fluorescence of the excited molecule. If the reaction proceeds by

⁷ Neujmin and Popov, *Zeits. f. physik. Chemie* **B27**, 15 (1934).

⁸ Flory and Johnston, *J. Am. Chem. Soc.* **57**, December (1935).

such a bimolecular process as an initial step, even under the optimum conditions of a collision efficiency of unity, the quantum yield must be less than 0.01, assuming no chain mechanism.⁹ It is very doubtful that such a low quantum yield could give rise to the rate of pressure decrease observed by Flory and Johnston. On the other hand, if one considers the reaction to depend on predissociation as the initial process this difficulty is overcome because for each quantum absorbed two oxygen atoms are produced. It is quite conceivable that subsequent reactions of these oxygen atoms cause the pressure decrease at the rate which has been observed. Thus, although this work does not elucidate the nature of secondary processes which occur when oxygen is irradiated under the conditions of the experiments, it does provide photochemical evidence which confirms the occurrence of predissociation independent of collisions.

These results in no way conflict with the view that the pressure decrease was due to a reaction of atomic oxygen kindred to that observed by Neujmin and Popov. Their failure to obtain any evidence of photochemical reaction caused by band absorption must have been due to the very much weaker absorption of oxygen in the banded region than in the continuum. Ladenburg and Van Voorhis² measured the absorption coefficient of oxygen in the continuum from 1700 to 1300 Å. By extrapolating their data to wave-lengths above 1750 Å one can see that at low pressures, where only a fraction of the total radiation at any wave-length is absorbed, the total absorption by the bands must be less than 1/50 of the total absorption in the continuum. This placed the rate of the photo-reaction at $\lambda > 1751$ below the limit of observation in the experiments reported by Neujmin and Popov. In the work of Flory and Johnston the use of a more intense source, the mercury arc, permitted the observation of the reaction in spite of weak absorption.

THE PREDISSOCIATION PROCESS

It is the implication of the above lines of evidence that oxygen molecules in $v' > 2$ levels of the

⁹ It is conceivable that the optically excited molecules might be dissociated by wall collision. However, at 0.1 mm pressure wall collisions occur much less frequently than bimolecular collisions. This mechanism would lead to a quantum efficiency less than 0.001.

$^3\Sigma_u^-$ state are destroyed at a rate much greater than the rate of fluorescence. Furthermore, this destruction process must be independent of collisions with other molecules if it is to explain satisfactorily Rasetti's observations on the fluorescence spectrum, the photochemical results just cited, and the absence of $v' > 2$ emission bands.¹⁰ Hence it must be a predissociation (independent of collisions; not a collision-dependent "induced predissociation"), and the transition to the repulsive electronic state responsible for it must obey Kronig's selection rules.¹¹

Before discussing the radiationless transition to the repulsive state which is responsible for the predissociation, it will be desirable to mention the predissociations which have been observed in molecules analogous to oxygen, i.e., other molecules formed from atoms in the sixth group of the periodic table. Bands analogous to the Schumann-Runge bands have been found in the spectra of the molecules S_2 , Se_2 , Te_2 , and SO . In each the transition is $^3\Sigma_u^- \leftrightarrow ^3\Sigma_g^-$ (in SO it is $^3\Sigma^- \leftrightarrow ^3\Sigma^-$, of course), the latter state being the normal state of the molecule. In each of these molecules except Se_2 a predissociation of the excited $^3\Sigma$ state has been found.¹² Hirschlaff¹³ has predicted that a similar predissociation of Se_2 occurs close to the convergence limit where its observation would be difficult.

The predissociations of the $^3\Sigma_u^-$ states of S_2 and Te_2 (and of Se_2 also according to Hirschlaff's

¹⁰ Runge does not state the pressure of the gas in the arc from which he photographed the emission spectrum, but unless it was much above 0.01 atmosphere, which is not likely, collision quenching could not prevent observation of these bands. On the other hand, Curry and Herzberg obtained their absorption spectrum at atmospheric pressure where the collision frequency is about 10^{10} per second. If a large fraction of the collisions of the activated molecules were effective in quenching them, it is conceivable that this quenching process would account for the broadened absorption lines.

¹¹ Jevons, *Report on Band-Spectra of Diatomic Molecules*, The Physical Society (London, 1932), p. 201. The selection rules for a radiationless transition derived by Kronig are, $\Delta\Lambda = \pm 1$ or 0, $\Delta\Sigma = 0$, $\Delta J = 0$, $++ \rightarrow +$ or $-- \rightarrow -$, and $g \rightarrow g$ or $u \rightarrow u$.

¹² Predissociation of S_2 , Christy and Naudé, *Phys. Rev.* **37**, 903 (1931); Te_2 , Hirschlaff, *Zeits. f. Physik* **75**, 315 (1932); SO , Martin, *Phys. Rev.* **41**, 167 (1932). In addition to these, induced predissociations of Se_2 and Te_2 (Heil, *Zeits. f. Physik* **74**, 18 (1932); Kondratjew and Lauris, *Zeits. f. Physik* **92**, 741 (1934)) have been found. The thresholds come at very low vibration levels, much below the thresholds for the ordinary predissociations.

¹³ Hirschlaff, *Zeits. f. Physik* **75**, 315 (1932).

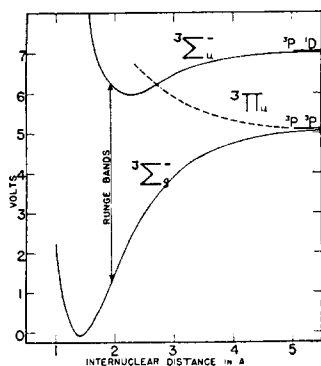


FIG. 2.

prediction) have been attributed to radiationless transitions to repulsive ${}^3\Pi_u$ states. This assignment was made on the basis of Kronig's rules¹¹ as follows. There are eighteen states which can be derived from two 3P atoms, one of which is the ${}^3\Sigma_g^-$ ground state. Radiationless transitions from a ${}^3\Sigma_u^-$ state to all of the remaining seventeen states except the ${}^3\Pi_u$ are forbidden. Therefore, the transition must be ${}^3\Sigma_u^- \rightarrow {}^3\Pi_u$. (In SO the transition is ${}^3\Sigma^- \rightarrow {}^3\Pi$.) For identical reasons the repulsive state responsible for the predissociation in oxygen must be ${}^3\Pi_u$ also. In Fig. 2 the ${}^3\Sigma_u^-$ and ${}^3\Sigma_g^-$ states are shown together with the repulsive ${}^3\Pi_u$ curve drawn to intersect the ${}^3\Sigma_u^-$ state at an energy between the second and third vibration levels. The relative positions of the three curves are similar to the analogs of O_2 discussed above.

In explaining the absence of bands in $\nu' > 2$ progressions in the emission spectrum and the low intensity of fluorescence in Rasetti's experiments it was shown that the probability of predissociation is much greater than the probability of fluorescence. The mean life of an excited molecule prior to fluorescence in the absence of predissociation is known to lie between 10^{-8} and 10^{-3} sec., and so the mean life of the excited state prior to predissociation must be $< 10^{-9}$ sec.

A crude estimate of this lifetime is possible if it be assumed that Curry and Herzberg's error (0.8 cm^{-1}) in measurement of the rotation lines in predissociation bands represents a satisfactory approximation of the line breadth. The lifetime, 10^{-11} to 10^{-10} sec., deduced in this manner is of the order of magnitude to be expected for a predissociation of this kind.

PHOTOCHEMICAL REACTIONS OF OXYGEN

Predissociation of oxygen in the region from about 1950 Å down to the convergence limit, 1751 Å, must release two unexcited 3P atoms, each with kinetic energy given by:

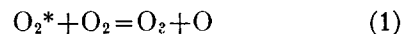
$$\text{K.E.} = 1/2(\bar{\nu} - 41,260) \times 1.234 \times 10^{-4} \text{ volts}$$

where $\bar{\nu}$ is the frequency of the quantum absorbed in wave numbers. Below 1751 Å one 3P and one 1D atom are the dissociation products, the kinetic energy of each atom being,

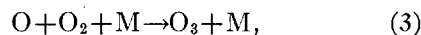
$$\text{K.E.} = 1/2(\bar{\nu} - 57,110) \times 1.234 \times 10^{-4} \text{ volts.}$$

Differences between the photochemical reactions of oxygen caused by light above and below the convergence limit must be due either to a difference in kinetic energy or to the difference in the reactivities of a 1D and a 3P oxygen atom. Certainly the latter difference is likely to be the more apparent.

Heretofore reactions of oxygen initiated by band absorption have been explained by postulating a collision of the optically excited molecule with a normal molecule as the first step. In view of the occurrence of predissociation the primary process must be the formation of atoms. For instance, in the formation of ozone which takes place with light above 1751 Å the reaction



(where O_2^* is an optically excited molecule) has been proposed.¹⁴ According to the present interpretation (1) must be replaced by the reactions:



where M is a third body necessary to stabilize the combination.¹⁵ Eq. (3) has been used previously in explanations of oxygen-ozone photo-kinetics.

¹⁴ This has been discussed by Noyes, Rev. Mod. Phys. 5, 280 (1933).

¹⁵ Professor G. B. Kistiakowsky has pointed out in a private communication that (1) is not necessarily ruled out if the rate of predissociation is less than the rate of collision. However, from the estimate of the life of the excited state prior to predissociation presented in the preceding section, the rate of predissociation can be no less than the rate of collisions at atmospheric pressure. Even if (1) occurs at every collision, which in itself is not likely, at atmospheric pressure (1) and (2) would be competing processes. At slightly lower pressures (2) would certainly predominate.