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Optical Dissociation of Iodine and Enhancement of Predissociation by Collisions

By Louis A. Turner
Palmer Physical Laboratory, Princeton University

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Optical dissociation of iodine molecules is demonstrated by absorption by the atoms of light of wave-lengths 1830, 1783, 1642, 1618, 1583 and 1515A these being the lines in the region 2100 to 1514 which arise from transitions to the normal state of the iodine atom. This dissociation is produced in iodine-argon mixtures by light of wavelength >5100A, which produces only excited molecules immediately upon absorption so that the atoms presumably result from dissociation produced by collisions. Spectra of electrical excitation and of fluorescence in iodine-argon mixtures show that molecules of higher v' are more effectively quenched, this larger quenching setting in at about $v'=12$. This suggests that the effect is a sort of predissociation, enhanced by collisions. A possible theoretical interpretation of such an effect is discussed.

SOME years ago[1] it was found possible to detect the optical dissociation of iodine *molecules* by observing the absorption of light by the iodine *atoms* resulting from this dissociation. The ultraviolet light from a discharge in iodine was passed through an absorption cell containing iodine which could be illuminated by the visible light from a carbon arc, and then into a small quartz spectrograph. The 1830 atomic line was less intense for those exposures during which the cell was illuminated by the visible light, because of its absorption by the iodine atoms produced in the absorption cell. It was suggested at that time that this arrangement might be of use in various experiments as a means of detecting the presence of iodine atoms, for it seems to be the only method so far discovered that will differentiate between iodine molecules and iodine atoms. Subsequent work on the magnetic quenching[2] of the fluorescence of iodine led to a theory which implies that the magnetic field produces atoms by means of a predissociation. It seemed desirable to try to verify this theory by demonstrating the production of the atoms by the magnetic field, and so work was begun in the endeavor to improve the absorption method of detecting atoms in order to make it a more useful tool for such researches. The experiments show that the method is not of as wide usefulness as originally hoped but various results were obtained which seem to be of sufficient interest to warrant publication.

EXPERIMENTAL METHOD

The three principal improvements in method in these experiments as compared with the former are in the use of a vacuum fluorite spectrograph, of a discharge at low pressures as light source in order to give narrow unreversed

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[1] Louis A. Turner, Phys. Rev. **31,** 983 (1928).
[2] Louis A. Turner, Zeits. f. Physik **65,** 464 (1930).

lines, and of argon in the absorption cell to slow down the diffusion of atoms to the wall. The iodine lines absorbable by atoms in the normal state lie for the most part in the Schumann region,[3] the one of longest wave-length being the line at 1830A. This latter line was the only one which could be observed with the old apparatus and then with difficulty, whereas several lines are usable with the new apparatus (see below). The vacuum spectrograph was one of the small ones described by Cario and Schmidt-Ott.[4] This method of the reversal of emission lines can be thought of as making it possible to do experiments of a sort ordinarily requiring high resolving power with spectroscopic instruments of low resolving power. The emission lines have automatically a distribution of energy in wave-length over the very narrow region of wave-length in which the absorption coefficient is large so that a large percentage of their energy is absorbable. A weakening of such lines can be observed quite readily by a small spectrograph with which it would be impossible to detect the absorption as fine black lines crossing a continuous background. The failure of Sponer and Watson[5] to observe the phenomenon may possibly thus be accounted for. That the condition be fulfilled it is necessary that the source of the emission lines be one which will give narrow and unreversed lines. For them to be narrow the source should be at a low temperature to make the Doppler width as small as possible, and the pressure should be low, which also minimizes self-reversal by reabsorption in the source. Such a source was obtained by exciting iodine at a pressure of 0.03 mm in a straight tube of a diameter of 8 mm by means of a high-frequency field from a short wave oscillator applied to two metal foils wrapped around the outside of the tube. Argon at various pressures up to 55 mm was put into the absorption cell in order to cut down the rate of diffusion to the walls of any iodine atoms formed. Inasmuch as the recombination of atoms to form molecules presumably takes place principally at the walls, this addition of argon ought to in-

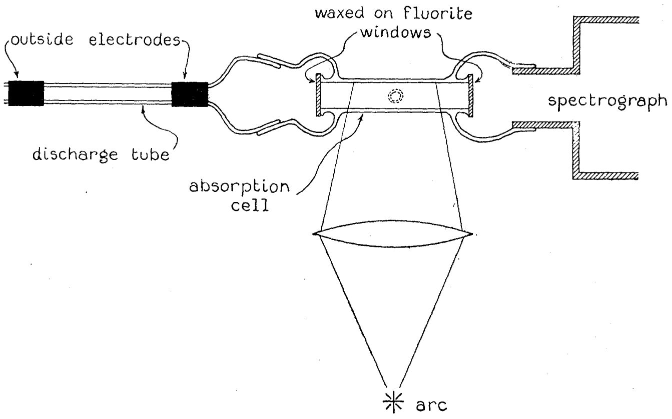

Fig. 1. Apparatus.

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[3] Louis A. Turner, Phys. Rev. **27**, 397 (1926).

[4] G. Cario and H. D. Schmidt-Ott, Zeits. f. Physik **69**, 719 (1931).

[5] H. Sponer and W. W. Watson, Zeits. f. Physik **56**, 184 (1929).

crease the concentration of atoms for any given rate of formation by slowing down the rate at which they leave the region of their formation. It was found, however, that the argon introduces further complicating effects which will be discussed below.

The absorption cell was illuminated by the light from a carbon arc run with a current of 13 amperes. It was focussed as an astigmatic bundle along the axis of the absorption cell by use of a suitable nonspherical lens. A diagram of the apparatus is given in Fig. 1.

RESULTS OF ABSORPTION EXPERIMENTS

Fig. 2 is a reproduction of a plate which shows the absorption clearly for the 1830, 1783 and 1642 lines. (1642 is the left hand line of the 1642–1641–1639 group.) Others made with longer exposures are more suitable for showing the effect with lines of shorter wave-length. For this one the pressure of the iodine in the absorption cell was 0.2 mm and that of the argon 50 mm.

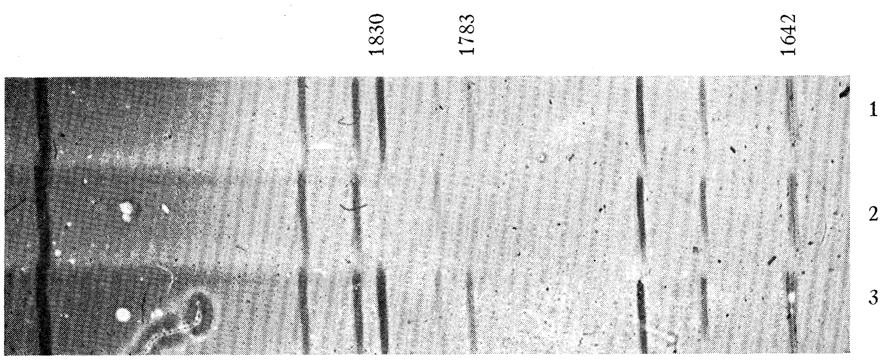

Fig. 2. Absorption by iodine atoms. Spectra 1 and 3, absorption cell not illuminated. Spectrum 2, absorption cell illuminated.

It has been pointed out previously[1] that the lines which arise from transitions to the normal state of iodine are known with practical certainty in spite of the fact that the spectrum has not yet been completely analyzed. Such lines appear as members of the shorter wave-length of doublets having the $\Delta\nu$ of the inverted ^2P term of the normal p^5 configuration (transitions from upper levels having J's of 1/2 and 3/2) or as single lines (transitions from upper levels having $J=5/2$). All other lines must be the long wave-length members of doublets (transitions to the $p^5\ ^2P_{1/2}$ level from upper levels having J's of 1/2 and 3/2) unless there be present unsuspected terms arising from other electronic configurations close to the $p^5\ ^2P$ term, which seems most improbable. In the region of the spectrum here investigated (2100–1514A) there are seven lines resulting from transitions to the normal $p^5\ ^2P_{3/2}$ level, of wave-lengths 1830, 1783, 1642, 1618, 1583, 1527, and 1515A. All of these, with the exception of 1527, have been observed to show the absorption. The result is, however, doubtful for 1583 as it is a relatively weak line appearing on only one plate and there showing but a very slight absorption. Three more lines than those given in the preliminary report of these experiments[6] have thus been found to show the absorption. No trace of it was noted with nine other lines in the region investigated, all of these being the members of longer wave-length of doublets.

According to the theory of optical dissociation[7] only light of wave-lengths falling in the region of the continuous absorption ($\lambda < 4995$A for iodine) should cause dissociation. This was tested by using filters to isolate different regions of the spectrum of the carbon arc. The absorption effect was obtained not only as expected when a filter was used transmitting light of wave-length less than 5100A (and some red light of $\lambda > 7600$ which is not strongly absorbed by I_2), but also, and indeed more strongly, when another filter which transmitted only light of wave-length greater than 5100A was used. The pressure of the iodine was 0.3 mm and that of the argon 53 mm in both experiments. With no argon present there was only slight absorption even with the full radiation, presumably because of the rapid diffusion of atoms to the walls where they recombine. This feebleness of the effect with iodine alone rather severely limits the range of usefulness of the method in the detection of iodine atoms and, in particular, makes it valueless in connection with experiments on the magnetic quenching.

The result of the experiment with light of wave-length greater than 5100A was a surprising one. Such light will upon absorption immediately produce excited molecules which, if isolated, reradiate the energy as fluorescence, as is well known. These excited molecules do, to be sure, contain an excess of energy over the energy of dissociation but the strength of the fluorescence indicates that few, if any, dissociate spontaneously rather than reradiate the absorbed energy. The absorption of the atomic lines with argon present indicates, therefore, either that these excited molecules dissociate upon collision with argon atoms or that the presence of the argon merely helps toward the building up of a concentration of iodine atoms resulting from a small percentage of spontaneous dissociation. If the latter be the case the argon should have little influence on the fluorescence. If the former be the true explanation then the argon should cause a considerable quenching of the fluorescence and the dependence of the magnitude of this effect upon the state of excitation of the molecule should be of interest.

Fluorescence Experiments

In view of these considerations experiments on fluorescence were undertaken. A tube was rigidly attached to a system so that argon could be admitted and pumped out without disturbing the optical arrangement. The source of the exciting light was a 400 watt tungsten lamp. The fluorescence light was photographed with an F3 Steinheil glass spectrograph. Exposures were made with argon at various pressures. Fig. 3 shows three such spectra on one plate chosen from several showing the same phenomenon. They were

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[6] Louis A. Turner and E. W. Samson, Phys. Rev. **37**, 1023A (1931).

[7] J. Franck, Trans. Faraday Soc. **21**, part 3 (1925).

taken on the same plate with conditions as indicated, and also printed together. The final enlarged prints all made in just the same way were then cut in order to place the spectra side by side. It is of interest that the spectrum shows a banded structure in spite of the fact that continuous light was used for the excitation. This results from the fact that of the many possible $v' \rightarrow v''$ transitions only a few have a relatively large transition probability, in particular, the $v' \rightarrow 0$ transitions for $v' > 16$. (See below on the electrically excited spectra.) The width of the bands results from the distribution of the molecules among the various rotation states. That such long exposures are necessary with the argon present indicates that there is an extinction of excited molecules of all values of v'. There is further an obvious greater quenching of the fluorescence at shorter wave-lengths. Since all absorbed energy must either be re-emitted as fluorescence or remain in the gas it is plain that the large quenching of the fluorescence indicates that the argon does have the effect of causing the excited molecules to dissociate. It is particularly noteworthy, however, that the quenching is greater for those molecules having a higher v'. It appeared from visual inspection that this increase of quenching set in at $v' = 29$ as was stated in the preliminary report[8] of these experiments. Subsequent work on these plates with a microphotometer, following apparently contradictory results by Loomis and Fuller discussed below, has shown that this result is illusory, the weakening of the bands appearing to begin in the neighborhood of $\lambda = 5710$A in fair agreement with their observations.

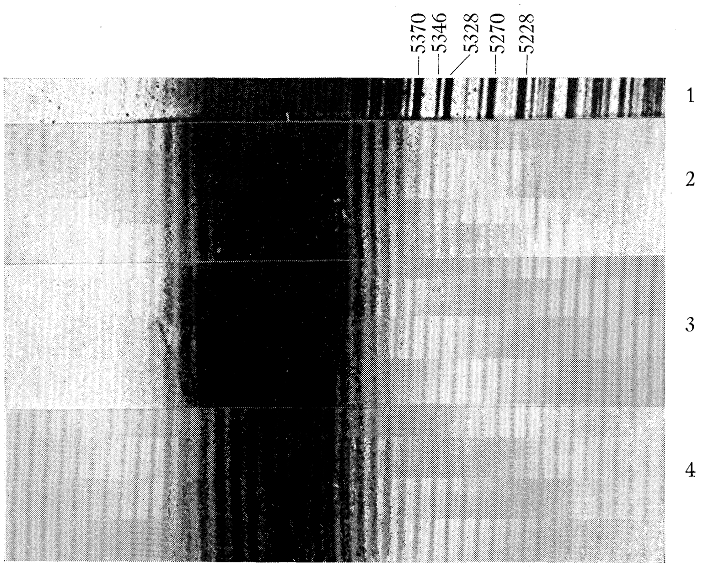

Fig. 3. Quenching by argon. (1) Fe arc; (2) iodine alone, 0.3 mm, 1 hr. 50 min; (3) iodine at 0.3 mm, argon at 11 mm, 4 hr., 45 min; (4) iodine alone, 0.3 mm, 1 hr. 20 min.

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[8] Louis A. Turner, Phys. Rev. **38**, 574 (1931).

ELECTRICALLY EXCITED SPECTRA

The general results of these experiments with fluorescence have been confirmed by other work done by the electrical excitation of the band spectrum of iodine in the pure vapor and in mixtures of it with argon. The same high-frequency excitation as used for the absorption experiments was found to be suitable although the light was rather weak. The iodine was kept at a pressure of 0.3 mm and argon at a pressure of 5 mm was used. In order to have the bands at longer wave-lengths at the same strength in the spectrum of the mixture as they were in the spectra of the pure iodine, exposures twelve times as long were needed. The same general result as that of the fluorescence experiment was obtained. For two exposures where the blackening of the plate for the bands of longer wave-length was the same in both, the bands at shorter wave-length (higher values of v') were weaker in the exposure made with the mixture. Examination of the plates with a microphotometer showed that this effect apparently begins with the bands at about 5900A and not at shorter wave-lengths as originally judged by inspection. These exposures were taken with a Hilger El glass spectrograph so that the band heads are nicely resolved. It is of interest that the only heads appearing with any strength are those of the bands observed by Mecke[9] in absorption. In particular for $v' > 16$, only the $v' \rightarrow 0$ of all possible $v' \rightarrow v''$ bands appear, thus emphasizing the fact of the much greater transition probability for the $v' \rightarrow 0$ transitions.

DISCUSSION OF EXPERIMENTS

The fluorescence experiment is merely a refinement of one done many years ago by Franck and Wood.[10] They observed the quenching of the iodine fluorescence by various gases including argon and noticed a reddening of the fluorescence light which corresponds to the greater quenching of the light of shorter wave-lengths noted above. Professor Franck suggested that the quenching might be the result of dissociation and that the reddening[11] was the result of the loss of vibrational energy excited molecules by collisions of the second kind with atoms of the admixed gas. The recent work of Heil[12] demonstrates the occurrence of this process in various molecules including iodine. Without additional hypothesis, however, this explanation does not suffice to account for the setting-in of increased quenching at any particular value of v'. It was for this reason that the author suggested[8] that these experiments gave evidence for an enhancement of a predissociation process by collision. Since the increase of quenching now appears to be not nearly so sudden as it originally seemed, this hypothesis might be considered questionable were it not for the experiments of Loomis and Fuller[13] on the absorption of mixtures of iodine with various gases. They found that with increase of

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[9] R. Mecke, Ann. d. Physik (4) **71**, 104 (1923).

[10] J. Franck and R. W. Wood, Phil. Mag. (6), **21**, 314 (1911).

[11] J. Franck, Ergebnisse der Exakten Naturwissenschaften **2**, 118 (1923).

[12] O. Heil, Zeits. f. Physik **74**, 18 (1932).

[13] F. W. Loomis and H. Q. Fuller, Phys. Rev. **39**, 180 (1932).

pressure of the admixed gas of various sorts, including argon, the absorption of light from a continuous background was relatively greater for wavelengths corresponding to $v' > 12$. They attributed this increased absorption to a relatively greater broadening of the absorption lines.[14] This broadening of the lines is what is observed in ordinary predissociation phenomena and corresponds to the shortening of the life of the molecule in the excited state. Loomis and Fuller independently arrived at the idea of predissociation caused by collision, their evidence being more convincing.

There remains the question as to why the collisions should produce predissociation. The author is not competent to develop a mathematical theory of the effect but would like to present for consideration an amplification of the suggestion previously made.[8] It has been pointed out[2,8] that there is a possibility of the occurrence of an ordinary natural predissociation in iodine vapor. The probability of it must be very small because the lines of the band spectrum of iodine are sharp. It would presumably have its probability increased by any influence which would tend to break down any of the selection rules. One of these is that J does not change, which is simply a quantum formulation of the law of the conservation of angular momentum, obviously applicable to a radiationless transfer in an isolated molecule. This principle should also be applicable to the more complicated system made up of an iodine molecule and an additional argon atom. The angular momentum of this system before collision can be conveniently thought of as being composed of the angular momentum of the iodine molecule about its own center of gravity plus that of the molecule and argon atom with respect to the center of gravity of the whole system. After collision and dissociation there will be three separate atoms and the total angular momentum will be the same. The part of it which can be thought of as associated with the motion of the two iodine atoms with respect to their mutual center of gravity need not, however, be the same as it was before the collision in order that the total angular momentum remain constant. The iodine molecule presumably loses its separate identity at the collision. This virtually amounts to a breaking down of the J selection rule of the predissociation which would tend to make the process a more probable one. A more detailed analysis might show that an initial probability for predissociation in the iodine molecule is not necessary, although it is difficult to see how an atom like one of argon in a $'S$ state could produce a change of the electronic states of the combined temporary triatomic molecule which would permit predissociation transitions otherwise impossible.

Since these fluorescence experiments with excitation by white light are very complicated in that excited molecules of all different vibration and

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[14] The author has found in conversations that there is considerable confusion about this matter. If k_ν be the absorption coefficient at frequency ν for a single line the absorbed energy will be represented by $E = I_0 \int_0^\infty (1 - e^{-k_\nu l}) d\nu$. Even though $\int_0^\infty k_\nu d\nu$ remains constant upon adding a foreign gas E will not necessarily do so. A simple consideration shows that if there is greater absorption at the center of the line, the total energy absorbed will be increased with a broadening of the line even though $\int_0^\infty k_\nu d\nu$ remains constant.

rotation quantum numbers are produced it seemed advisable to proceed next to a study of the quenching by argon and other gases of the fluorescence excited by approximately monochromatic radiation. Such work has been in progress here during the past year but is not yet completed. Various complicating factors, the importance of which was not realized at the outset, have had to be taken into account. The transfer effect, i.e., the loss of vibrational energy upon collision is more probable than was at first realized, the reabsorption of the fluorescent light in the tube must be considered, the widening of the absorption lines changes the amount of energy absorbed from the beam of exciting light and this must be measured in order to make the measured apparent quenching be of significance,[15] the auto-quenching by other iodine molecules is also of sufficient magnitude to influence the results. Clean-cut, significant quantitative results concerning the effect of the added gas are thus difficult to get and it remains to be seen what the final degree of success in the experiments will be.

For his skill and perseverance my thanks are due to my former assistant, Dr. E. W. Samson, who did practically all of the experimental work here reported.

Note added in proof, August 13, 1932. A recent paper by V. Kondratiew and L. Polak (Zeits. f. Physik **76,** 386 (1932)) describes experiments showing the influence of added oxygen on the absorption spectrum of bromine vapor and NO_2. They also suggest the occurrence of predissociation produced by collision with bromine and show that the oxygen added to NO_2 increases the predissociation already present with NO_2 alone. The present author suggests that the effects observed with iodine and perhaps also with bromine may well be of this latter sort, the natural predissociation being, however, much less prominent.

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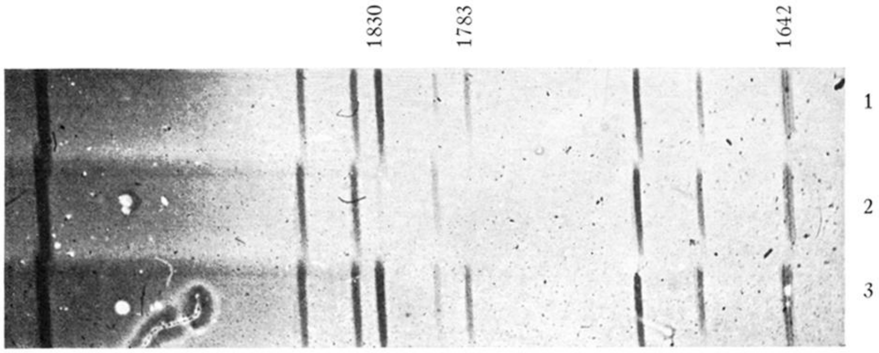
[15] The importance of this consideration in such work has recently been emphasized by L. v. Hámos, Zeits. f. Physik **74,** 379 (1932).



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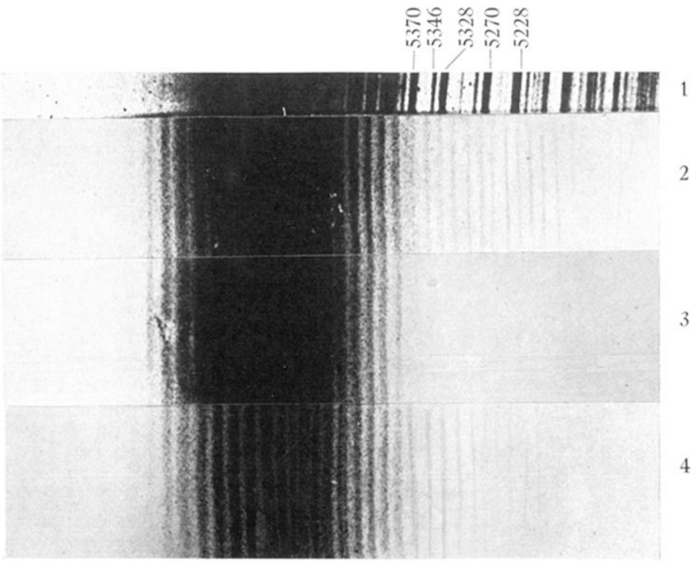

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