THE RESONANCE LINE OF THE IODINE ATOM AND THE OPTICAL DISSOCIATION OF IODINE MOLECULES

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Abstract

The resonance line of the iodine atom is most probably that of wave-length 1830.4A, corresponding to a resonance potential of 6.75 volts. Light of that wave-length is absorbed by a cell containing iodine vapor more strongly when it is illuminated by concentrated light from a carbon arc than when it is not so illuminated. The increased absorption is attributed to iodine atoms produced by the illumination, in accord with Franck's theory of optical dissociation.

THE absorption spectrum of iodine in the visible region consists of sequences of bands which are closer together on the side of shorter wave-lengths and converge to a limit at 4995A, beyond which there is a region of continuous absorption. Franck[1] suggested that absorption of light in this region results in the dissociation of I_2 molecules into separate I atoms, one in the normal state, the other in a metastable excited state. This theory was supported by the experiments of Dymond[2] who found that when light of wave-length longer than 4995 was absorbed fluorescence light was re-emitted but that when light of wave-lengths in this continuous region was absorbed there was no fluorescence, as would be the case if the two atoms were separated. Kuhn[3] investigated the absorption spectra of bromine and chlorine, finding them to be of the same sort, and showed that the heat of dissociation for each substance as calculated by Franck's theory agreed with that determined by thermal methods, within the experimental accuracy of the latter. Thus, there could be very little doubt as to the correctness of Franck's theory. Nevertheless, it seemed that it might be of interest to demonstrate the dissocation by an experiment which would indicate the presence of the iodine atoms directly. A consideration of the probable absorption spectrum of the iodine atom showed that the absorption of light of the proper wave-length could be used as a distinctive and delicate test for the presence of the atoms.

The Resonance Line of Iodine

A line spectrum of iodine has not been observed in absorption nor has the spectrum of emission lines been completely analyzed, but it is possible to conclude from very general considerations that light of the wave-lengths of certain of these lines must be absorbed by the normal atoms. According to Hund's theory, the normal electronic configuration of a halogen atom

[1] J. Franck, Trans. Faraday Soc. **21**, part 3 (1925); and Zeits. f. Phys. Chem. **120**, 144 (1926).

[2] E. G. Dymond, Zeits. f. Physik **34**, 553 (1925).

[3] H. Kuhn, Zeits. f. Physik **39**, 77 (1926).

gives an inverted ^2P term. A recurring frequency difference between lines of the arc spectrum of iodine in the Schumann region has been found,[4] and is most probably the frequency difference between these two levels of the P term. The term being inverted, the j value of the lower and normal level is 3/2, that of the upper is 1/2. Any upper level which combines with these will, if its j is 3/2 or 1/2, give two lines having the $\Delta\nu$ characteristic of the lower levels. If its j is 5/2 it can combine only with the lower level, the j of which is 3/2. A level with j equal to 7/2 or more can combine with neither of the low levels. The line of shorter wave-length of each pair having the frequency difference of the ^2P term would therefore be absorbed by normal atoms. Further, any line in the region of the spectrum of lines involving jumps to the low ^2P levels which is single (i.e., has no companion with a $\Delta\nu$ characteristic of the low ^2P levels) must be connected with jumps from a higher state for which $j=5/2$ to the normal level for which $j=3/2$, and light of that wave-length must be absorbable by atoms in the normal state.

The iodine line of this latter sort of longest wave-length is the exceedingly strong 1830.4 line. It is, most probably, the $a^2P_{3/2}-k^4P'_{5/2}$ line[5] which is predicted by Hund's theory to be the single line of longest wave-length, as follows. The low ^2P term comes from the p^5 configuration. The next higher terms must come from the p^4s configuration which gives $^4P'$, $^2P'$, ^2S, and ^2D terms. Of these the $^4P'$ and the $^2P'$ should be much the lowest, the $^4P'$, somewhat lower than the $^2P'$, and both inverted. These predictions have been fulfilled in the spectra of Ne^+ and A^+, recently analyzed.[6] The lowest level of all of this group is the $^4P'_{5/2}$ which, combining with $^2P_{3/2}$, most probably gives the 1830.4 line. The other strong lines of longer wave-lengths, viz., 2062.1, 1876.4, 1844.5, are emitted by transitions to the $^2P_{1/2}$ level. 1830.4 is therefore the resonance line of the atom, corresponding to a critical potential of 6.75 volts. This value is in better agreement with Kondratjew[7] and Leipunsky's measured value of 6.5 volts than the previously suggested value of 6.92 volts, which is the energy of excitation of the upper level involved in the emission of the strong 2062.1 and 1782.9 lines.

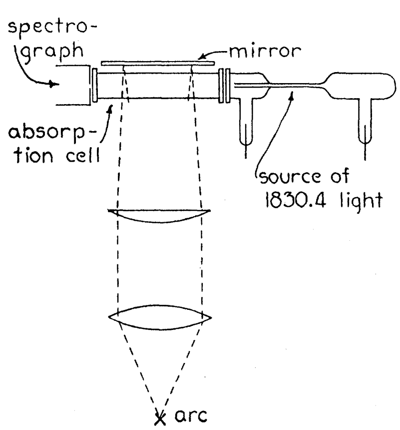

Fig. 1. Arrangement of apparatus.

THE OPTICAL DISSOCIATION OF IODINE

Light of a wave-length of 1830.4A should therefore be absorbed by iodine atoms and can be used to detect their presence. The apparatus was arranged as shown in Fig. 1. The source of the 1830.4 light was a discharge tube of the form indicated in the figure, with a quartz win-

[4] L. A. Turner, Phys. Rev. **27**, 397 (1926).
[5] Bowen's notation. I. S. Bowen, Phys. Rev. **29**, 231 (1927).
[6] H. N. Russel, K. T. Compton and J. C. Boyce, Proc. Nat. Acad. Sci. **14**, 280, 1928.
[7] A. Kondratjew, and A. Leipunsky, Zeits. f. Physik **44**, 708, 1927.

dow, containing iodine, and excited by a small transformer. The absorption cell was of glass with quartz windows at the ends. It was connected to the pumps through liquid air traps. An appendix containing iodine was usually left at room temperature so that the maximum vapor pressure of iodine was 0.2 mm. Light from a strong carbon arc could be concentrated upon it by lenses, the second of which gave an astigmatic bundle focussed in a line along the axis of the cell. The spectrograph was a small Hilger quartz spectrograph which had been readjusted for work with light of these shorter wave-lengths. Commercial nitrogen from a tank was flowed through it continually so as to eliminate the absorption by the oxygen of the air in the region of the shorter wave-lengths. Schumann plates were used.

It was found that other things being equal, the intensity of the 1830.4 line on the plate was cut down decidedly by the illumination of the iodine in the absorption cell by light from the arc. The 1844.5 and 2062.1 lines were not so absorbed, showing that the $^2P_{1/2}$ metastable atoms produced in the optical dissociation must quickly revert to the normal $^2P_{3/2}$ state. One would expect that they would do so by collisions of the second kind with iodine molecules. This absorption produced by illumination was superposed upon a considerable absorption by molecular iodine in this region. In order to show that the increase of absorption produced by illuminating the tube is absorption of a very narrow region of the spectrum by atoms, rather than an increase of absorption in the whole region, light from a Geissler tube containing CO_2 was passed through the cell instead of that from the tube containing iodine. This tube gave, with great intensity, the CO bands found by Schumann. One of these has its head on the side of shorter wave-lengths at 1830.2A and is wide enough to serve as a continuous background over a range of wave-lengths including that of the iodine line. Indications of an absorption line produced by the illumination of the cell were obtained but not with sufficient regularity and reliability to be at all certain. This is not surprising since the absorption of the line from the iodine tube, of just the right wave-length, was not great, although quite definite. The experiments with the CO band gave no indication, however, of an increase in the general absorption in the neighborhood of the 1830.4 line. The conclusion is that the absorption produced by the illumination of the cell is absorption of a very narrow region at 1830.4A, exactly that predicted for iodine atoms, and therefore an indication of the production of these atoms by the light.

The results of the experiment are thus in agreement with the theory of the optical dissociation of iodine, and with the conclusion that the 1830.4 line of the atom is the resonance line. It indicates the usefulness of this optical method for detecting small quantities of iodine atoms.

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