NOTE ON THE VISIBLE HALOGEN BANDS, WITH SPECIAL REFERENCE TO ICl

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Abstract

It is pointed out that the dissociation of excited ICl molecules, after absorption of light in the visible bands, into normal atoms is in harmony with theory. In analogy with the other halogens, these bands probably belong to a $^3\Pi \leftarrow {}^1\Sigma^+$ transition. The upper level of the bands is, however, doubtless not just the 0^+ part of the $^3\Pi_0$ as in the homonuclear halogen molecules, but is probably the whole $^3\Pi_0$, or else the $^3\Pi_1$. Detailed arguments against the possibility that the upper state of the halogen bands may be $^3\Sigma$ are given. Conclusions drawn in previous papers from the behavior of the I_2 bands in magnetic fields are revised.

IN TWO previous papers,[1,2] the writer has shown that the well-known visible absorption bands of the molecules Cl_2, Br_2, and I_2 probably correspond to the transition $0^+{}_u(^3\Pi) \leftarrow {}^1\Sigma^+{}_g$. The object of the present note is to supplement these papers by extending their application to such molecules as ICl, and by revising two or three doubtful or erroneous statements made in them.

Interpretation of ICl Bands

In molecules like ICl, relations between molecular and atomic electron states somewhat different from those in I_2 or Cl_2 are to be expected. This is obvious from the fact that we have four combinations $I(^2P_{1\frac{1}{2}})+Cl(^2P_{1\frac{1}{2}})$, $I(^2P_{1\frac{1}{2}})+Cl(^2P_{\frac{1}{2}})$, $I(^2P_{\frac{1}{2}})+Cl(^2P_{1\frac{1}{2}})$, and $I(^2P_{\frac{1}{2}})+Cl(^2P_{\frac{1}{2}})$, where with I_2 we have only three. Besides, it can hardly be taken for granted that the electronic states of the molecule ICl should show any close analogy to those of I_2 or Cl_2. Nevertheless, experience with other molecules shows that such an analogy may be expected (cf. analogies of SO to S_2 and O_2, CS and SiO to CO, AlO to BO, etc.).

A clearer understanding can be obtained by attempting to assign electron configurations. It has been assumed[2] that the normal and excited states of the visible absorption bands of chlorine are . . . $4d\sigma^2 3p\pi^4 4d\pi^4$, $^1\Sigma^+{}_g$ and . . . $4d\sigma^2 3p\pi^4 4d\pi^3 5f\sigma$, $^3\Pi_u$ (inverted) and that the corresponding states of I_2 are . . . $6d\sigma^2 5p\pi^4 6d\pi^4$, $^1\Sigma^+{}_g$ and . . . $6d\sigma^2 5p\pi^4 6d\pi^3 7f\sigma$, $^3\Pi_u$. It seems likely that the normal and excited states of the visible ICl bands have exactly the same configurations of outer electrons as I_2, the outer Cl electrons being promoted to equality with those of the I atom. Such a promotion appears necessary, since all the orbits which the outer electrons would occupy in Cl_2 are already filled in the I atom of ICl. This argument then supports the analogy already men-

[1] R. S. Mulliken, Phys. Rev. **36**, 699 (1930).

[2] R. S. Mulliken, Phys. Rev. **36**, 1440 (1930).

tioned. The $^3\Pi$ excited state of ICl, like those of the other halogens, should in view of its electron configuration be *inverted*. The triplet width should probably be about the same as in the $^3\Pi$ of Br_2, for which 2400 cm^{-1} seems a reasonable estimate.

It has been shown[1] that in I_2 the upper state of the visible bands is probably a 0^+_u state and that on theoretical grounds such a state cannot possibly be derived from $I(^2P_{1\frac{1}{2}})+I(^2P_{1\frac{1}{2}})$ or $^2P_{\frac{1}{2}}+^2P_{\frac{1}{2}}$, but that it can be derived from $^2P_{1\frac{1}{2}}+^2P_{\frac{1}{2}}$, as is observed. It was also shown to be likely that this 0^+_u belongs to a $^3\Pi$ state (mentioned in the preceding paragraph) of which the 0^-_u, 1_u, and 2_u components theoretically can and probably do dissociate into unexcited atoms. In the case of ICl, however, because of the absence of the property indicated by g or u, there is no theoretical reason why the 0^+ component of a $^3\Pi$ state analogous to that of I_2 should not dissociate, like the 0^-, 1, and 2 components, into normal atoms. In fact the theory makes this probable,—although it does not require it.

For according to the rules giving the relations between case c molecular and atomic states,[2] we may expect the following correlations : case c states 3, 0^+, 0^-, 2, 1, 2, 1, 1, 0^+, 0^- from $I(^2P_{1\frac{1}{2}})+Cl(^2P_{1\frac{1}{2}})$; 2, 1, 1, 0^+, 0^- from $I(^2P_{1\frac{1}{2}})+Cl(^2P_{\frac{1}{2}})$ and a similar set from $I(^2P_{\frac{1}{2}})+Cl(^2P_{1\frac{1}{2}})$; 1, 0^+, 0^- from $I(^2P_{\frac{1}{2}})+Cl(^2P_{\frac{1}{2}})$. These are the same sets of states that one gets from $2I(^2P_{1\frac{1}{2}})$; $I(^2P_{1\frac{1}{2}})+I(^2P_{\frac{1}{2}})$; and $2I(^2P_{\frac{1}{2}})$, respectively, except for the fact that no indices g or u are assigned here. It will be seen that all the case c states 2, 1, 0^+, and 0^- necessary to give a $^3\Pi$ state in case a can be obtained from two normal atoms $I+Cl$. Now there has been a good deal of discussion as to whether the upper state of the visible ICl bands gives two normal atoms on dissociation or whether it gives an excited chlorine atom.[3] The experimental evidence[3] strongly favors the latter alternative, which is here seen to be in harmony with theory. (It also negatives the possibility that an excited iodine atom is formed on dissociation.)

Assuming that the ordinary visible ICl bands give two normal atoms on dissociation, the question may still be raised as to whether their upper level is really the 0^+ component of a $^3\Pi_0$ as in I_2. First it should be noted that, if 0^+ is stable, it should be accompanied by 0^-, forming a complete $^3\Pi_0$, since if 0^+ dissociates into normal atoms, the corresponding 0^- almost certainly does too. Next comes the question whether this $^3\Pi_0$ should be a stable molecular state. If one examines Fig. 2 of Ref. 2, it will be seen that the fact that 0^+_u of I_2 is a reasonably stable molecular state (dissociation energy 0.55 volts) is due largely to the fact that it gives an excited atom on dissociation. Fig. 2 indicates that the 0^- and even the $^3\Pi_1$ and $^3\Pi_2$ components of the $^3\Pi_u$ should be much less stable in I_2 than the 0^+, or perhaps not be real molecular states at all. In view of these relations, one may question whether the $^3\Pi_0$ state of ICl should be stable, since it dissociates giving normal atoms. It therefore seems worth while,—although of course the quantitative relations may be considerably different than in Cl_2, Br_2, and I_2,—to consider the possibility that the upper level of the ICl bands may be $^3\Pi_1$ or even $^3\Pi_2$, and that the $^3\Pi_0$ state gives rise only to a continuum. [It is, however, also theoretically possible, although im-

probable, that both components of the $^3\Pi_0$ state might give excited atoms on dissociation, so that $^3\Pi_0$ would be a higher but stable state.] A possible indication that the upper level of the ICl bands is not $^3\Pi_0$ as in the other halogens is the fact that its energy (1.69 volts above the ground state)[3] is lower than that of any of the other halogens, while its dissociation energy (0.47 volts[3]) is nearly as large as that of I_2. If, however, it should turn out after all to be $^3\Pi_0$, then one should probably find at longer wave-lengths other bands leading to $^3\Pi_1$ and perhaps also to $^3\Pi_2$.

ADDITIONS AND CORRECTIONS TO PREVIOUS PAPERS

Possibility that the upper level of the halogen bands is $^3\Sigma$. A possible interpretation of the visible halogen bands which was not entirely disposed of in Refs. 1 and 2 was that they belong to a $^3\Sigma^+_u$ (case b), $^1\Sigma^+_g$ transition with $\Delta K = \pm 1$ in which only those combinations having $\Delta J = \Delta K = \pm 1$ are observed, the other possible combinations $\Delta J = 0$ being for some unknown reason very weak. This reason might possibly be found in the intersystem character of $^3\Sigma \leftarrow ^1\Sigma$, for whose intensity relations we have no reliable guiding theory. [But as was mentioned in Ref. 1(p. 701), we know that in the $^1\Sigma \leftarrow$ $^3\Sigma$ atmospheric oxygen bands, the transitions with $\Delta J = 0$ are as strong as those with $\Delta J = \pm 1$, and there seems no reason why the same should not be true here. Nevertheless since it is likely[4,5] that the atmospheric bands are $^1\Sigma^+_g \leftarrow ^3\Sigma^-_g$, the argument may not hold, since this is a quadrupole transition.] A rather strong argument is that there is no theoretical necessity here for a $^3\Sigma^+_u$ state (which becomes 0^-_u plus 1_u in case c) to give $^2P_{1\frac{1}{2}} + ^2P_{\frac{1}{2}}$ on dissociation, as the upper levels of the halogen bands are empirically known to do, whereas in the case of a 0^+_u state such a necessity does exist. [There is, to be sure, no theoretical proof that such a $^3\Sigma^+_u$ state could *not* give $^2P_{1\frac{1}{2}} + ^2P_{\frac{1}{2}}$ here, although the theory strongly favors $^2P_{1\frac{1}{2}} + ^2P_{1\frac{1}{2}}$ as dissociation products.[2]] A consideration of electron configurations also strongly favors a 0^+_u state (belonging to a $^3\Pi_0$) as against a $^3\Sigma^+_u$ state.[2]

Granting that the upper level of the halogen bands is 0^+_u, this might still conceivably be a 0^+_u which, together with a 1_u, would go over for small r into a case b $^3\Sigma^-_u$ state.[2] But a consideration of possible electron configurations makes this very improbable; at least two excited electrons would be required. Everything considered, it seems very probable that the identification of the upper state of the halogen bands as a 0^+_u belonging to a $^3\Pi_0$ is correct.

Magnetic behavior of iodine bands. In Ref. 1 the fact that a $^3\Pi_0$ molecular gas should be paramagnetic was taken as an explanation of the Faraday effect

[3] G. E. Gibson and H. C. Ramsperger, Phys. Rev. **30**, 598 (1927); E. D. Wilson, Phys. Rev. **32**, 611 (1928); G. E. Gibson and O. K. Rice, Nature, March 9, 1929; G. E. Gibson, Zeits. f. Physik **50**, 692 (1928); J. Patkowski and W. E. Curtis, Trans. Faraday Soc. **25**, 725 (1929); W. E. Curtis and O. Darbyshire, Trans. Faraday Soc. **27**, 77 (1931). G. K. Rollefson and F. F. Lindquist, J. Am. Chem. Soc. **52**, 2793 (1930); **53**, 1184 (1931).

[4] R. S. Mulliken, Phys. Rev. **32**, 880 (1928).

[5] R. S. Mulliken, Phys. Rev. 1931 (Abstract, Washington Meeting, Spring, 1931). Recent work of Childs and Mecke (Zeits. f. Physik **68**, 344, 1931) gives extremely low absorption coefficients in the atmospheric bands, and so favors $^1\Sigma^+_g$ rather than the possible alternative $^1\Sigma^-_u$ as the upper state of these bands.

observed in the iodine bands. Unfortunately, however, the fact was over-looked that the observed Faraday effect indicates that the normal state of iodine ($^1\Sigma^+{}_g$) is magnetically rather more sensitive than the upper ($0^+{}_u$) state.[6] The fact was also overlooked that, although a $^3\Pi_0$ molecular gas should be paramagnetic (less so, however, if the $^3\Pi_0$ is widely split into 0^+ and 0^-), this does not imply a first-order Zeeman effect. In fact, the 0^+ and 0^- states belonging to a $^3\Pi_0$ state should behave, if well-separated, very much like $^1\Sigma$ states in respect to the Zeeman or Faraday effect; but if the separation of the 0^+ and 0^- states should be small and if, as is the case for low K values in I_2, the separations of the rotational levels should be less than the spacing of the components of a normal Zeeman triplet, a magnetic field should produce a Paschen-Back effect in the $^3\Pi_0$ levels.[7]

But unless there is an error in Kemble's conclusion that the normal more than the excited state is responsible for the observed Faraday effect, we should probably return to Kemble's explanation[6] of this effect in the iodine bands, namely, that it is caused by the development of a small magnetic moment through the rotation of the molecule. Its existence would then really give no evidence either for or against the $^3\Pi_0$ nature of the upper electron level in the iodine bands. Nevertheless a renewed investigation of the matter would be of interest.

The quenching of the fluorescence of the iodine bands in a magnetic field, emphasized in Ref. 1, seems to indicate a special sensitiveness of the upper level to magnetic fields. The most promising suggestion as to the cause of the magnetic quenching of fluorescence seems to be Turner's idea[8] that it is due to a magnetically induced predissociation.

Indeed Van Vleck has now found, in a paper soon to be published, that a magnetic field may be expected to induce predissociation in the 0^+ state belonging to a $^3\Pi_0$ when the 0^+ and 0^- components dissociate as shown in Fig. 2 of Ref. 2. Thus the existence of magnetic quenching gives strong evidence in favor of the designation $0^+{}_u(^3\Pi_0)$.

[6] Cf. E. C. Kemble, Nat. Research Council Bulletin on Molecular Spectra, p. 347.

[7] The writer is indebted to Professor J. H. Van Vleck for the elucidation of these points. Cf. J. H. Van Vleck, Phys. Rev. **31**, 587 (1928).

[8] L. A. Turner, Zeits. f. Physik **65**, 477 (1930).