

ELECTRONIC STATES IN THE VISIBLE HALOGEN BANDS

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(Received July 7, 1930)

ABSTRACT

It is shown on the basis of theoretical considerations that the well-known visible iodine absorption bands and the analogous bands of the other halogens almost certainly cannot correspond to a ${}^1\Sigma \leftarrow {}^1\Sigma$ transition as hitherto supposed. It is concluded that they belong to a ${}^3\Pi_{0u} \leftarrow {}^1\Sigma_g^+$ transition, with a case c ${}^3\Pi_0$ state whose Λ -type doubling is so wide that the state is split into two separate states which simulate a ${}^1\Sigma_u^+$ and a ${}^1\Sigma_u^-$ state. The observed bands involve however only the state which behaves like ${}^1\Sigma_u^+$, the ${}^1\Sigma_u^-$ -like state and the ${}^3\Pi_1$ and ${}^3\Pi_2$ states being unknown. The classification ${}^3\Pi_0$ really has little meaning, one needs for case c here a classification in which only Ω values and symmetry properties (+ or -, g or u) are significant. According to the above interpretation, the upper level of the halogen bands is paramagnetic, this is in harmony with certain magnetic phenomena observed with these bands. Electron configurations for the normal and excited states are suggested in the case of fluorine.

TWO identical atoms in the same 2P state¹ are capable, as one finds by applying the relations obtained by Wigner and Witmer,² of giving only the following set of molecular states: ${}^1\Delta_g, {}^3\Delta_u, {}^1\pi_u, {}^1\pi_g, {}^3\pi_u, {}^3\pi_g, {}^1\Sigma_g^+, {}^1\Sigma_g^+, {}^1\Sigma_u^-, {}^3\Sigma_u^+, {}^3\Sigma_u^+, {}^3\Sigma_g^-$. As we shall see, this is almost certainly⁵ in conflict with the current interpretation of the visible absorption bands of iodine and the analogous bands of the other halogens as ${}^1\Sigma, {}^1\Sigma$ transitions. The argument is as follows.

For convenience we shall speak in terms of the *chlorine* bands, since our knowledge is more well-rounded for these than for the bands of the other halogens. What is said is intended to apply to all the halogens, since there can scarcely be a doubt that the bands of the four molecules are all of the same type. In respect to some properties, the iodine bands are better known than the chlorine bands, but we shall feel free to apply this knowledge also to the latter. (1) That the *normal state* of Cl_2 is ${}^1\Sigma$ seems assured by the fact that chlorine gas is diamagnetic (Br_2 and I_2 are also known to be diamagnetic in the *liquid* state). This conclusion is strongly supported by a study of

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¹ For the prediction of the possible molecular states as given above, the division of the 2P normal state into ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$ substates does not matter, by the "normal state" of the atom we mean either ${}^2P_{\frac{1}{2}}$ or ${}^2P_{\frac{3}{2}}$ or both.

² E. Wigner and E. E. Witmer, *Zeits. f. Physik* **51**, 883 (1928). The designations Σ^+ and Σ^- used here correspond to Wigner and Witmer's Σ and Σ^1 (also to their 0 and 0'). The subscripts g and u (gerade and ungerade) mean "even" and "odd". In the case of odd (even) states the electronic factor of the wave-function ψ does (does not) change sign on reflection in the midpoint of the line joining the nuclei. $\Sigma_g, \Pi_u, \Delta_g$ are respectively the same as $\Sigma_+, \pi_+, \Delta_+$ of Wigner and Witmer, while $\Sigma_u, \Pi_u, \Delta_u$ are the same as their $\Sigma_-, \Pi_-, \Delta_-$.

possible electron configurations for the normal molecule.³ (2) That this ${}^1\Sigma$ state is either a ${}^1\Sigma_g^+$ or a ${}^1\Sigma_u^-$ state is shown by the fact that the rotational levels with odd values of K have the greater statistical weight.^{4,5} Either ${}^1\Sigma_g^+$ or ${}^1\Sigma_u^-$ is capable,—see above,— of being derived from two normal atoms.¹ Whether or not the normal states of the halogens *actually are* so derived is not essential to the present argument, but is nevertheless of interest. By extrapolation from the known vibrational levels of the normal state, as in the method of Birge and Sponer, one gets, for I_2 , Br_2 and Cl_2 , values of the energy of dissociation which agree well with the supposition that dissociation does give normal atoms.¹ Also, since all excited states of the atoms (including $F^+ + F^-$) lie high above the normal level, it is improbable that any of these could give normal atoms. (3) A consideration of possible electron configurations consistent with ${}^1\Sigma_g^+$ and ${}^1\Sigma_u^-$ shows that only ${}^1\Sigma_g^+$ is reasonable for the normal state of the halogens.⁶ But even if we should

³ A ${}^3\Pi_1$ state would also be diamagnetic, but such a state is very unlikely to be the normal state, since the correspondence ${}^3\Pi_2$ would probably also exist and be lower, assuming case a coupling, ${}^1\Sigma$ is also by far the most probable normal state on the basis of a study of electron configurations.

⁴ That the odd levels have the greater weight is shown in the case of Cl_2 by the band analysis of A. Elliot (Proc. Roy. Soc. **123A**, 629, 1929). In the case of Br_2 an analysis of the bands is lacking, while in I_2 no alternations in intensity have been detected. If we represent the complete wave function ψ as a product of three factors, $\psi = \psi_{el}\psi_{rot}\psi_{nu..pin}$, then we know (a) ψ must on theoretical grounds (cf. R. S. Mulliken, Trans. Faraday Soc. No. 102, **25**, Part II Nov. 1929) be antisymmetrical in the nuclei (An)⁵; (b) for the levels with greater statistical weight in any homonuclear molecule, $\psi_{nu..pin}$, is always symmetrical in the nuclei (Sy), for odd values of K in a Σ state, ψ_{rot} , is always An . For the odd K values, therefore, in Cl_2 ψ_{rot} , is An , $\psi_{nu..pin}$, is Sy , hence, since ψ itself must be An , ψ_{el} must be Sy . This is the case for either a Σ_g^+ or a Σ_u^- state. (The possibility of Σ^- states was overlooked in the writer's article just cited, and led to some erroneous conclusions in regard to O_2 , whose normal state is now known to be ${}^3\Sigma_g^-$.)

⁵ That the complete ψ must be An for a molecule whose nuclei contain each an odd number of (protons plus electrons), as theoretically predicted by Hund (cf. R. S. Mulliken, Ref. 4), is contradicted by the experimental results on N_2 , where ψ is Sy although the nucleus is composed of 21 particles (14 protons, 7 electrons). The most probable reformulation is that ψ has to be An if the nucleus of each atom contains an odd number at *protons* (and Sy if it contains an even number), regardless of the electrons. Since both the old and the new conditions for an An ψ are fulfilled for the Cl atom, it seems safe to take this for granted. If, however, the contrary should be true, the following results would hold: the normal Cl_2 molecule is ${}^1\Sigma_u^+$ or ${}^1\Sigma_g^-$ (both are improbable on the basis of a consideration of electron configurations), and dissociates giving at least one highly excited atom (this would hardly be possible to reconcile with data on the vibrational levels (cf. section (2) in the text above)), the excited molecule would then probably be ${}^1\Sigma_g^+$ or Σ_u^- , either of which is derivable from normal atoms¹, in agreement with section (5) in the text.

⁶ It is highly probable that the normal state of F_2 is a ${}^1\Sigma_g^+$ state with essentially the following electron configuration: $1s\sigma^2 p\sigma^2 2s\sigma^2 3p\sigma^2 3d\sigma^2 2p\pi^4 3d\pi^4$. Possible ${}^1\Sigma_u^-$ states are derivable from $\dots 2p\pi^3 3d\pi^3 n x \sigma^2$ (n and x anything not already present) and $\dots 2p\pi^4 3d\pi^3 3p\pi$. The first of these (probably with $n x \sigma^2 = 4f\sigma^2$) might be derived from two normal atoms, but would surely be higher and be more unstable than the ${}^1\Sigma_g^+$ configuration mentioned above. The second ($\dots 3p\pi$) could probably be obtained only from one normal F atom and one excited atom with a $3p$ electron; the energy of excitation of the latter would be so great that it practically certainly could not give the normal state of F_2 . Analogous arguments apply to the other halogens.

assume ${}^1\Sigma_u^-$, we should still come to the conclusion that the halogen bands here under discussion cannot be a ${}^1\Sigma, {}^1\Sigma$ transition. (4) Assuming that the normal state is ${}^1\Sigma^g$ and that the coupling relations in both states correspond to Hund's cases *a* or *b*, the *excited state* can only be one of the following:⁷ ${}^1\Sigma_u^+$, or ${}^1\pi_u$, or ${}^3\Sigma_u^+$, or ${}^3\Pi_u$. (5) According to Franck's well-known interpretation of the convergence limits of the halogen bands, the excited state dissociates without question into two normal atoms,—more accurately, into one ${}^2P_{3/2}$ and ${}^2P_{1/2}$ atom. (6) Since a ${}^1\Sigma_u^+$ state cannot possibly be obtained from two normal atoms (cf first paragraph), the excited state cannot possibly be ${}^1\Sigma_u^+$, and the bands therefore cannot be of the ${}^1\Sigma, {}^1\Sigma$ type. The possibilities ${}^1\Pi_u$, ${}^3\pi_u$, and ${}^3\Sigma_u^+$ for the excited state remain, since all are consistent with dissociation into normal atoms.

None of the interpretations ${}^1\pi \leftarrow {}^1\Sigma$, ${}^3\pi \leftarrow {}^1\Sigma$, and ${}^3\Sigma \leftarrow {}^1\Sigma$ appear easy to reconcile with the observed structure of the bands, which (in Cl_2 and I_2 , F_2 and Br_2 not having been investigated as yet) consists definitely only of one *P* and one *R* branch, each composed of single lines arranged exactly as in the case of a ${}^1\Sigma, {}^1\Sigma$ transition. The absence of a *Q* branch probably rules out the possibility of a ${}^1\Pi$ upper level. ${}^3\Pi$ also seems unlikely unless its combinations with ${}^1\Sigma$ are restricted, say, to one component of the ${}^3\Pi_0$ level (see below). In favor of ${}^3\Sigma_u^+$ is the fact that in a ${}^3\Sigma \leftarrow {}^1\Sigma$ transition only a *P* and an *R* branch are expected. But one would expect these to consist of wide doublets as in the ${}^1\Sigma \leftarrow {}^3\Sigma$ atmospheric oxygen bands.⁸ That the observed lines are single seems hardly reconcilable with a ${}^3\Sigma, {}^1\Sigma$ combination. One might of course suppose that the ${}^3\Sigma$ rotational triplets are so narrow as to be unresolved, but, especially for the heavier halogens, this is wholly contrary to theory, as well as to experimental data on doublet separations in ${}^2\Sigma$ states. Another conceivable explanation would be that in the ${}^3\Sigma$ level the components with $J=K \pm 1$ are widely separated from those with $J=K$ and that, for unknown reasons, only combinations of the levels with $J=K$ with levels of the ${}^1\Sigma_g^+$ normal state are observed. This would give simple *P* and *R* branches in agreement with experiment, but it is very far-fetched.

An escape from these difficulties is to be found by noting a fact whose consequences have hitherto not been fully appreciated. In the excited states of the halogen molecules, the energies of dissociation *D* are very small ($D=0.55$ volts for I_2 , 0.39 volts for Br_2 , 0.23 for Cl_2 , and by extrapolation from the other halogens, about 0.1 volts for F_2); they are roughly about equal to the doublet separations between the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ sublevels of the normal states of the halogen atoms (I, 0.94 volts, Br, 0.45 volts, Cl, 0.11 volts, F, 0.05 volts). From these figures we can conclude that, especially in the heavier halogens, the influence of the electric axis on the electron orbits

⁷ The following selection rules apply if both states correspond to coupling cases *a* or *b* or intermediate cases: $\Delta \Lambda = 0, \pm 1$; Σ^+ terms combine with Σ^+ but never with Σ^- terms; in homonuclear molecules, even terms (*g*) combine only with odd terms (*u*). Quintet states are ruled out, for the excited state, by the fact that the latter dissociates into normal atoms (cf. list of possible states in first paragraph).

⁸ R. S. Mulliken, *Phys. Rev.* **32**, 880 (1928).

is not large enough to break down, at any rate not at all completely, the coupling of each atomic L vector with its S vector. The quantum numbers $L_1, S_1, J_1, L_2, S_2, J_2$ of the two atoms still retain their significance to a considerable extent in the molecule. J_1 and J_2 give respectively quantum numbers Ω_1 and Ω_2 (or M_1 and M_2) which represent their projections on the electric axis. The only electronic quantum number which is significant for the molecule as a whole is Ω ($\Omega = |M_1 + M_2|$). Λ and S for the molecule as a whole are practically meaningless as quantum numbers; λ 's of individual electrons are even more completely lacking in significance; nevertheless Λ, S , and λ values can be formally assigned by imagining the nuclei pushed closer together. This coupling case can be classified as a form of Hund's case c ; in another form which has been more discussed, the molecule as a whole has an L and an S , which are strongly coupled to give a resultant J^a , which in turn gives a projection Ω .

For the *normal* states of the halogen molecules, where the D values are moderately large (assuming dissociation into two $^2P_{1/2}$ normal atoms, they are, $D = 1.53$ volts for I_2 , 1.96 volts for Br_2 , 2.54 for Cl_2 , and by extrapolation, about 3.1 volts for F_2), we may assume Hund's case a , or in I_2 perhaps a case intermediate between a and c .

In dealing with the present weak-binding form of case c , it seems best to designate different electronic states simply by numbers giving their Ω values (0, 1, 2, etc.), together with a superscript $+$ or $-$ when $\Omega = 0$ and a subscript g or u in the case of homonuclear molecules in order to designate certain symmetry properties of their ψ functions. Here g and u have the same meaning as in cases a and b . So do $+$ and $-$, but for convenience we may here define 0^+ and 0^- states as follows: in 0^+ states the even-numbered rotational levels ($J = 0, 2, \dots$) are even (in the sense of Kronig) or positive (in the sense of Wigner and Witmer), while the odd-numbered levels are odd or negative;⁹ in 0^- states the relations are reversed.¹⁰

As selection rules in case c here we have only the following: $\Delta\Omega = 0, \pm 1$; $\Delta J = 0, \pm 1$; $g \rightleftharpoons u$; even or positive combine only with odd or negative rotational levels. The intensity relations in the P, Q , and R branches should be governed, just as in case a , by the Hönl and London intensity formulas.¹¹ For example, transitions between a 0 and a 1 state should show a P , a strong Q , and an R branch. (The 1 state should have Ω -type doubling, vanishing with zero rotation, and similar to the Λ -type doubling for a $^1\Pi$ state in cases a and b ; and the P and R branches should make connection with one component of each Ω -type doublet, the Q branch with the other). Transitions

⁹ The words "even" [R. de L. Kronig, *Zeits. f. Physik* **50**, 351 (1928)] and "positive" (Wigner and Witmer, ref. 2, 867, footnote) are here synonymous; likewise for "odd" and "negative".

¹⁰ For a discussion of the behavior of $^3\Pi_0$ states in the passage from case a to case c , cf. J. H. Van Vleck, *Phys. Rev.* **33**, 501-2 (1929). Van Vleck points out that the a and b sets of sublevels of $^3\Pi_0$ behave like a $0^+, 0^-$ pair (similar to $^1\Sigma^+$ and $^1\Sigma^-$). In regard to notation use of $+$ and $-$) cf. ref. 2.

¹¹ H. Hönl and F. London, *Zeits. f. Physik* **33**, 803 (1925) Cf. R. S. Mulliken, *Phys. Rev.* **29**, 391, (1927) for discussion and applications.

between two 0 states should show only a P and an R branch, just as for ${}^1\Sigma$, ${}^1\Sigma$ transitions in case a . This latter fact, taken in connection with the selection rule even \rightleftharpoons odd for rotational terms, shows that only combinations between two 0^+ states, or between two 0^- states, but not those between a 0^+ and a 0^- state, are capable in case c of giving rise to spectrum lines.¹² In case, however, there should be a departure from the conditions of case c toward those of case a , Q branch combinations between a 0^+ and a 0^- state may also be expected (cf. next paragraph).

Let us now consider as a typical example, for a range of cases from a to c , a transition which in case a would be classified as ${}^3\Pi_0$, ${}^1\Sigma$. The ${}^3\Pi_0$ state has two rotational levels for each J value ($J=0, 1, 2, \dots$); these may be considered as derived from two electronic sublevels of ${}^3\Pi_0$, namely from a 0^+ and a 0^- sublevel.¹¹ In case a , we may probably expect a P , a Q , and an R branch in a ${}^3\Pi_0$, ${}^1\Sigma$ combination. For a ${}^1\Sigma^+$ type of ${}^1\Sigma$ state, the P and R branches come from the 0^+ levels of the ${}^3\Pi_0$, the Q branch from the 0^- levels. In the passage to case c , the P and R branches remain, but the Q branch $0^-, 0^+$ combination should gradually fade out, while at the same time the 0^- levels may become widely separated¹¹ from the 0^+ levels.

In both limiting cases (a and c), and probably also in intermediate cases, the rotational energy for the ${}^3\Pi_0$ states is given by an expression of the form $E = \text{const.} + B_v J(J+1) + \dots$. The same expression for E_r also holds for all electronic states in case c , as well as in case a .

We are now in a position to interpret the halogen bands from a more general viewpoint than that adopted at the beginning of this paper. Their observed structures show that they are a $0 \leftarrow 0$ transition; more specifically, since we have seen that the lower state is in all probability a ${}^1\Sigma_g^+$ and since they consist of P and R branches, we conclude that they are $0_u^+ \leftarrow 0_g^+$. As we have already seen, the 0_u^+ state cannot correspond to a ${}^1\Sigma_u^+$ state, since such a state is not derivable from normal atoms. In the list of states derivable from normal atoms (cf. first paragraph of paper), *only one* 0_u^+ state is to be found, namely the 0^+ component of the ${}^3\Pi_u$ state,¹³ and we therefore conclude that the upper level of the halogen bands is of this type. The absence of a Q branch corresponding to the 0^- component of ${}^3\Pi_u$ can be understood (cf. preceding paragraph) in view of the fact that we expect case c coupling here for the 0_u^+ state. It may even be that the 0_u^- state is much more unstable than the 0_u^+ , so that the corresponding band system $0_u^- \leftarrow 0_g^+$ (Q branches) may consist only of a continuous region: furthermore, it may be that this system is very weak.—It should be emphasized that the classification of the 0_u^+ level as belonging to ${}^3\Pi$ has only a formal meaning, since

¹² This is analogous to, but not (except in singlet states) identical with the rule that in combinations between Σ states only Σ^+, Σ^+ and Σ^-, Σ^- are possible.

¹³ The other 0 states derivable from two equal 2P atoms are, 0^- from ${}^3\Pi_u$, 0^+ and 0^- from ${}^3\Pi_g$, two 0_g^+ states and one 0_u^- state corresponding to the three ${}^1\Sigma$ states (one of the 0_g^+ states is the normal ${}^1\Sigma_g^+$ state of the molecule), and two 0_u^- and one 0_u^+ state from the two ${}^3\Sigma_u^+$ states and the one ${}^3\Sigma_u^+$ state respectively. A ${}^3\Sigma^+$ state gives in case c , as is easily shown, one 0^- and one 1 state; a ${}^3\Sigma^-$ state, one 0^+ and one 1 state (cf. later paper).

quantum numbers Λ and S are not defined here in case c . Physically, this 0_u^+ level may have little resemblance to a ${}^3\Pi_0$ ordinary level of case a .

By application of the methods of Wigner and Witmer, it is possible to predict, for a loosely-bound case c molecule as here, the molecular states which can be derived from each of the individual combinations ${}^2P_{1\frac{1}{2}}+{}^2P_{1\frac{1}{2}}$, ${}^2P_{1\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{1}{2}}{}^2P_{\frac{1}{2}}$.¹⁴ The results are, for the case of two equal atoms in the same 2P state: ${}^2P_{1\frac{1}{2}}+{}^2P_{1\frac{1}{2}}$ gives $3_u, 2_g, 2_u, 1_u, 1_g, 1_u, 0_g^+, 0_u^-, 0_g, 0_u^-$; ${}^2P_{1\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ gives $2_g, 2_u, 1_g, 1_u, 1_g, 1_u, 0_g^+, 0_u^+, 0_g^-, 0_u^-$; and ${}^2P_{\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ gives $1_u, 0_g^+, 0_u^-$.¹⁵ The fact that only ${}^2P_{1\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ is capable of giving a 0^+ state is in satisfying agreement with the experimental fact that the upper level of the halogen bands, here classified as 0_u^+ , is actually derived from ${}^2P_{1\frac{1}{2}}+{}^2P_{\frac{1}{2}}$. The lower, 0_g^+ , level is probably derived from ${}^2P_{1\frac{1}{2}}+{}^2P_{1\frac{1}{2}}$, although ${}^2P_{1\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ or ${}^2P_{\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ is not theoretically impossible, and also experimentally not yet absolutely excluded.

Some additional items of evidence having a bearing on the above interpretation of the halogen bands will now be mentioned. (1) The fact that the I_2 bands show a Faraday effect¹⁶ may be cited as evidence in favor of a paramagnetic upper level. Now it can be shown that a case c molecular state with $\Omega=0$ and derived from a ${}^2P_{1\frac{1}{2}}$ plus a ${}^2P_{\frac{1}{2}}$ atom *should* be paramagnetic; and that in the passage to a case a ${}^3\Pi_0$ state, the paramagnetism must increase.¹⁷ Of course, as Kemble has pointed out,¹⁶ a magnetic moment might be developed by rotation, even in a ${}^1\Sigma$ state; and in a loosely bound molecular state such as we have here, a rather large moment might be developed in this way through uncoupling of the atomic J vectors from the electric axis. But it seems hardly likely that the small rotational energies involved in the case of the observed band lines are large enough to give rise to the magnetic effects observed. (2) The fact that the fluorescence of the I_2 bands is (in part) quenched by a magnetic field¹⁸ is further evidence in favor of a paramagnetic upper level. (3) If the bands are ${}^3\Pi_0\leftarrow{}^1\Sigma$ one might expect their intensity to increase markedly in going from F_2 to I_2 , since the intensity of intersystem combinations is extremely weak for the lightest atoms like He,

¹⁴ The rules which govern this case, and some applications, will be discussed in a subsequent paper.

¹⁵ The group of states here predicted corresponds, as of course it must if correct, in a one to one manner to the set of states predicted by the Wigner and Witmer method for cases a and b , and given at the beginning of this paper. E.g., 3_u from ${}^2P_{\frac{1}{2}}+{}^2P_{\frac{1}{2}}$ corresponds to $\Omega=3$ of ${}^3\Delta_u$ at case a .

¹⁶ Cf. E. C. Kemble, Nat. Research Council Bulletin on Molecular Spectra, p. 347.

¹⁷ To get a state with $\Omega=0$ from ${}^2P_{\frac{1}{2}}+{}^2P_{1\frac{1}{2}}$, we must assume the J of the ${}^2P_{1\frac{1}{2}}$ atom oriented with a projection $M=\pm 1/2$ on the electric axis, the J of the ${}^2P_{\frac{1}{2}}$ atom with a projection $M=\mp 1/2$. Since Landé's g factor is $4/3$ for ${}^2P_{1\frac{1}{2}}$ and $2/3$ for ${}^2P_{\frac{1}{2}}$, the total magnetic moment parallel to the electric axis is $(4/3 \times 1/2 - 2/3 \times 1/2) = 1/3$ Bohr magneton. This holds for the limiting case of very loose coupling of the atoms. In a case a ${}^3\Pi_0$ state, we have a magnetic moment of ± 2 magnetons parallel to the electric axis due to the spin ($S=1, \Sigma=-1$) and of ∓ 1 magnetons due to $\Lambda=1$, making a net result of 1 magneton parallel to the electric axis. (The magnetic moment component perpendicular to the electric axis also in some cases contributes to the paramagnetism.)

¹⁸ W. S. Steubing, Ann. d. Physik **58**, 55 (1919).

and increases with the intensity of the coupling of L and S vectors. The fact that the upper level is case $c0^+$ rather than case $a^3\Pi_0$ should however probably diminish this effect since the molecular S loses its meaning in case c , but it might well still exist to a more or less marked extent, since it is likely that case a is more nearly approached in the lighter than in the heavier molecules. In the halogen bands in which we are interested, the spectrum consists of two parts, namely the bands proper (relatively weak), and the continuum (stronger). Since the continuum corresponds to transitions with r near r_e'' , and since we probably have case a for $r=r_e''$, the upper level should function here as a true $^3\Pi_0$ level, and the strong variation of intensity with molecular weight which is to be expected for intersystem combinations should make itself evident here. Experimentally the intensity of the bands proper increases rather rapidly in the order F_2 to I_2 , but this is at least partly explainable in terms of the $U'(r)$ and $U''(r)$ curves by means of the Franck idea as applied by Condon. So far as can be judged from available data,¹⁹ the absorption in the continuum is however also much stronger for iodine than for chlorine, and this effect cannot be attributed to the nature of the $U(r)$ curves. This relation is therefore in harmony with our expectation.

(4) If one assigns the electron configuration $1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3d\sigma^2 3d\pi^4$ to the $^1\Sigma_g^+$ normal state of F_2 , and assumes that the excited state corresponds to $\dots 3d\pi^3 4f\sigma$ one removes the only known exception²¹ to the writer's λ conservation rule (formerly called " $\sigma_{l,r}$ conservation rule") for molecule formation (Of course the configurations given here have a physical meaning only, for small values of the distance between the nuclei.) The writer is, however now inclined to believe that this rule has not much significance. For Cl_2 the corresponding configurations are $\dots 3s\sigma^2 4p\sigma^2 3p\pi^4 4d\sigma^2 4d\pi^4$ and $\dots 4d\pi^3 5f\sigma$ and so on.

¹⁹ Cf. International Critical Tables Vol. V, p. 269. The nature of the intensity relations can be judged by the following values of the absorption coefficient K in the equation $I = I_0 e^{-Kl}$ (l = length of absorbing path in cm, in gas or vapor). For the maximum of the continuous absorption, K has the following values: Cl_2 , $K \sim 2$ for $p = 760$ mm at $0^\circ C$; Br_2 , $K \sim 1.36$ for $p = 66$ mm at $16^\circ C$; I_2 , $K \sim 0.21$ for $p = 0.17$ mm (reduced to $0^\circ C$) and $K \sim 0.77$ for $p = 1.67$ mm (reduced to $0^\circ C$). If we assume the validity of Beer's law (but the data on I_2 show that it does not hold) we get for $p = 1.67$ mm at $0^\circ C$, $K \sim 0.013$ for Cl_2 , $K \sim 0.033$ for Br_2 , $K \sim 0.77$ for I_2 .

²⁰ R. S. Mulliken, Phys. Rev. **32**, 772 (1928).