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# The Halogen Molecules and Their Spectra. *J–J*-Like Coupling. Molecular Ionization Potentials

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The relations between molecular and atomic ionization potentials are discussed, and rules are formulated, differing for non-bonding, bonding, and anti-bonding electrons. Comparisons are made between ionization potential values predicted by these rules and observed values for $N_2$, CO, $X_2$, HX (X = halogen). Rather good agreement is found. Electron configurations of these molecules and $O_2$ are discussed. The low-energy states of the halogen ions $X_2^+$ and $(XY)^+$ are discussed, and some of their properties are predicted. With this as a background, low-energy excited states of $X_2$ and XY are discussed. Many new low-energy states are predicted (Tables III and IV), some giving halogen atoms both in unexcited electron configurations on dissociation, others giving one atom with an excited electron. The foregoing predictions are used to give a reasonable interpretation of the observed absorption spectra of the XY and $X_2$ molecules, extending into the vacuum ultraviolet. Suggestions are also made for interpreting observed fluorescence and emission spectra. The *D* level of $I_2$ is shown to be probably analogous to the $1s\sigma 2p\sigma$, ${}^1\Sigma^+_u$ state of $H_2$, with a wave function corresponding to $I^-(\sigma^2\pi^4)I^+(\pi^4)$. The vacuum ultraviolet bands of XY observed by Cordes and Sponer in the regions mainly λλ1600–1950 are of particular interest. The interpretation of an observed interval in these bands leads to the conclusion that the upper levels are in each case of the type $[X^+Y, {}^2\Pi_{1\frac{1}{2}}]\sigma^\times$ and $[X^+Y, {}^2\Pi_{\frac{1}{2}}]\sigma^\times$, with $\Omega$–$s$ (*J–J*-like) coupling between the $X^+Y$ core and the $\sigma^\times$ excited electron. Nearly $\Omega$–$s$ coupling is also present, according to the multiplet intervals, in the upper levels of the visible and infrared $I_2$, $Br_2$, ICl and IBr absorption bands. The possibility is discussed that part of the intensity in the continua associated with these bands belongs to an expected ${}^1\Pi\leftarrow{}^1\Sigma^+$ transition.

## I. MOLECULAR ELECTRON CONFIGURATIONS AND IONIZATION POTENTIALS

### 1. Electron configurations of diatomic molecules

A few years ago the writer tentatively suggested a theoretical interpretation of the visible and near-visible absorption spectra of the halogen molecules,[1] which subsequent experimental[2,3] and theoretical[4] work has supported. The present paper deals mainly with a further development of this interpretation, including an extension to bands farther in the ultraviolet.

The theoretical treatment involves two aspects: (*a*), interpretation of electronic states in terms of electron configurations, and prediction of their properties; and (*b*), dissociation product correlations. The new development is chiefly in the former direction. We follow here mainly the Lennard-Jones procedure of assigning unshared electrons to atomic orbitals, shared electrons to molecular orbitals. In practice, the principal difficulty is in drawing the line properly between shared and unshared electrons. In border-line cases, it is useful to write down the electron configuration twice, with the doubtful electrons assigned in each of the two ways, then to study the implications of each, and perhaps to interpolate.

According to the writer's present judgment, the following represent the best formulations for the lowest-energy electron configurations of some typical diatomic molecules. Electrons inside the valence shell are omitted. In the case of the halogens (X, Y, with Y heavier than X and $n=2$, 3, 4, 5 for F, Cl, Br, I), the atomic states which would result on dissociation are also given.

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[1] R. S. Mulliken, Phys. Rev. **36**, 699, 1440 (1930); **37**, 1412 (1931); Rev. Mod. Phys. **4**, 17, 70 (1932). Cf. W. Weizel, *Bandenspektren*, W. Jevons, *Report on Band Spectra*, and Kayser and Konen, Handbuch der Spectroscopie, especially Vol. VII, Part 3 (1934), for numerous references on the halogen spectra, not given here.

[2] Visible and infrared bands of $Br_2$, $I_2$: W. G. Brown, Phys. Rev. **37**, 1007; **38**, 1179, 1187 (1931). For $U(r)$ curves cf. also R. S. Mulliken, Rev. Mod. Phys. **4**, 17 (1932), Fig. 42.

[3] Visible and infrared **ICl** bands: O. Darbyshire, Phys. Rev. **40**, 366 (1932); W. E. Curtis and J. Patkowski, Phil. Trans. Roy. Soc. **232**, 395 (1933); and especially W. G. Brown and G. E. Gibson, Phys. Rev. **40**, 529 (1932) and reference 4; cf. also O. K. Rice, J. Chem. Phys. **1**, 375 (1933); for intensity data, G. E. Gibson and H. C. Ramsperger, Phys. Rev. **30**, 603 (1927), also W. E. Curtis and O. Darbyshire, Trans. Faraday Soc. **27**, Part 2, p. 77, (1931). Also other papers cited by the foregoing writers. **IBr**, R. M. Badger and D. M. Yost, Phys. Rev. **37**, 1548 (1931); H. Cordes, Zeits. f. Physik **74**, 34 (1932); W. G. Brown, Phys. Rev. **42**, 355 (1932). $U(r)$ curves, cf. also reference 9.

[4] J. H. Van Vleck, Phys. Rev. **40**, 544 (1932), especially pp. 553–4: theory concerning $I_2$ and ICl; R. Schlapp, Phys. Rev. **39**, 806 (1932): band structures.

$$\mathrm{N}_2:\quad \left.\begin{array}{ccccl} \cdots(s+s,\ \sigma_g)^2 & (s-s,\ \sigma_u)^2 & (\pi+\pi,\ \pi_u)^4 & (\sigma+\sigma,\ \sigma_g)^2, & {}^1\Sigma^+{}_g \\ {[30]} & 18.8 & (16.3) & 15.6 & \\ \{>24.8\} & \{<24.8\} & \{>13.45\} & \{>14.1\} & \end{array}\right\}, \tag{1}$$

$$\mathrm{CO}:\quad \left.\begin{array}{cccccl} \cdots(2s_{\mathrm{O}})^2 & (s_{\mathrm{C}}+\sigma_{\mathrm{O}},\ \sigma)^2 & (\pi_{\mathrm{O}}+\pi_{\mathrm{C}},\ \pi)^4 & (\sigma_{\mathrm{O}}-s_{\mathrm{C}}\pm\sigma_{\mathrm{C}},\ \sigma)^2, & {}^1\Sigma^+ \\ & 19.7 & 17.1 & 14.3 & \\ \{32\} & \{\text{see text}\} & \{\text{see text}\} & & \end{array}\right\}, \tag{2}$$

$$\mathrm{O}_2:\quad \left.\begin{array}{cccccl} \cdots(2s)^2 & (2s)^2 & (\sigma+\sigma,\ \sigma_g)^2 & (\pi+\pi,\ \pi_u)^4 & (\pi-\pi,\ \pi_g)^2, & {}^3\Sigma^-{}_g,\ {}^1\Delta_g,\ {}^1\Sigma^+{}_g \\ & \{32\} & {[18]} & {[16]} & {[11.5]} & \end{array}\right\}, \tag{3}$$

$$\mathrm{X}_2:\quad \left.\begin{array}{cccl} \cdots(\sigma+\sigma,\ \sigma_g)^2 & (np\pi)^4 & (np\pi)^4, & {}^1\Sigma^+{}_g \longleftrightarrow \text{two X}: \cdots(np)^5,\ {}^2P_{1\frac{1}{2}} \\ \{>I^\circ{}_{\mathrm{X}}\} & \{\text{near } I^*{}_{\mathrm{X}}\} & & \end{array}\right\}, \tag{4}$$

$$\mathrm{XY}:\quad \left.\begin{array}{cccl} \cdots(\sigma_{\mathrm{Y}}+\sigma_{\mathrm{X}},\sigma)^2 & (n_{\mathrm{Y}}p\pi)^4 & (n_{\mathrm{X}}p\pi)^4, & {}^1\Sigma^+ \longleftrightarrow \mathrm{Y}: (n_{\mathrm{Y}}p)^5,\ {}^2P_{1\frac{1}{2}} + \mathrm{X}: (n_{\mathrm{X}}p)^5,\ {}^2P_{1\frac{1}{2}} \\ \{>\mathrm{I}^\circ{}_{\mathrm{Y}}\} & \{\text{near } I^*{}_{\mathrm{Y}}\} & \{\text{near } I^*{}_{\mathrm{X}}\} & \end{array}\right\}, \tag{5}$$

$$\mathrm{HX}:\quad \left.\begin{array}{ccl} \cdots(\sigma_{\mathrm{X}}+s_{\mathrm{H}},\ \sigma)^2 & (n_{\mathrm{X}}p\pi)^4, & {}^1\Sigma^+ \longleftrightarrow \mathrm{X} : (np)^5,\ {}^2P_{1\frac{1}{2}} + \mathrm{H} : 1s,\ {}^2S \\ \{>I^\circ{}_{\mathrm{X}}\} & \{\text{near } I^*{}_{\mathrm{X}}\} & \end{array}\right\} \tag{6}$$

Below each type of orbital is given a number or symbol indicating the ionization potential in volts for removing one electron. These apply to non-adiabatic ionization processes in which the distance between the nuclei is not changed (Franck-Condon maximum of probability). Hereafter we shall refer to such potentials as *vertical* ionization potentials, since they correspond to vertical lines on a diagram of potential energy curves. The numbers given in (1) to (6) are largely based on critical potential and spectrum data; values in parentheses or (more uncertain) brackets are, however, estimates, or else based on interpretations which are not certain or ($\pi_g$ of $O_2$) averages. These are compared with *predicted* values given in curly braces { }; in regard to the latter, and the meaning of $I^*$ and $I^\circ$, cf. section 2, where are also given observational data on ionization potentials of the halogens (Table I).

Although the use of atomic orbitals for the $\pi$ electrons in (4) gives without much doubt the best approximation, there is nevertheless undoubtedly an appreciable—possibly a strong—tendency toward an approximation (4*a*) using molecular orbitals:

$$\mathrm{X}_2: \begin{array}{ccc} \cdots(\sigma+\sigma,\ \sigma_g)^2 & (\pi+\pi,\ \pi_u)^4 & (\pi-\pi,\ \pi_g)^4,\ {}^1\Sigma^+{}_g. \\ \{>I^\circ{}_{\mathrm{X}}\} & \{>I^*{}_{\mathrm{X}}\} & \{<I^*{}_{\mathrm{X}}\} \end{array} \tag{4a}$$

In previous papers by the writer, the approximation (4*a*) has usually been used. A strong tendency toward (4*a*) would mean a considerable difference between the two ionization potentials $\pi_u$ and $\pi_g$ of (4*a*). Unfortunately no direct evidence on this point now exists, but it is likely that a continued study of the halogen spectra will give this.—Similar remarks apply to (5) and the corresponding (5*a*), but the tendency toward (5*a*) should be less than toward (4*a*).

XY:

$$\cdots(\sigma_{\mathrm{Y}}+\sigma_{\mathrm{X}},\ \sigma)^2(\pi_{\mathrm{Y}}+\pi_{\mathrm{X}},\ \pi)^4(\pi_{\mathrm{X}}-\pi_{\mathrm{Y}},\ \pi)^4,\ {}^1\Sigma^+. \tag{5a}$$

In the electron configurations (1) to (6), each parenthesis encloses a symbol which denotes a particular type of atomic or molecular orbital. These symbols are simplest for the homopolar molecules $N_2$, $O_2$, $X_2$. Here atomic orbitals are given by simple symbols such as $2s$, $np\sigma$, $np\pi$, and molecular orbitals by such symbols as $(s+s,\ \sigma_g)$ and $(\pi+\pi,\ \pi_u)$. Each of these is made up of an informal and particular part, such as $(s+s)$, $(\sigma+\sigma)$, $(\pi+\pi)$, these being abbreviations for $(2s + 2s)$, $(np\sigma + np\sigma)$, $(np\pi + np\pi)$, and a *systematic*, internationally accepted, designation such as $\sigma_g$ or $\pi_u$. The informal symbols are roughly descriptive of the individual forms of the orbitals, e.g. $(2s + 2s)$ means a form which could be (somewhat roughly) approximated—as suggested by Hund—by forming the normalized sum of two $2s$ atomic orbitals, one located on each of the atoms.

In earlier papers, the writer and others have used various other symbols for molecular orbitals, such as $2s\sigma$, $\sigma_g 2s$, $z\sigma_g$ for $(2s + 2s, \sigma_g)$; $2s\sigma'$, $\sigma_u 2s$, $y\sigma_u$ for $(2s - 2s, \sigma_u)$, $2p\pi$, $\pi_u 2p$, $w\pi_u$ for $(2p\pi + 2p\pi, \pi_u)$. The present informal symbols are introduced here for purposes of maximum momentary clearness and convenience. They could be improved by elaboration, e.g. $(s+s, \sigma_g)$ of $N_2$ could be written more accurately as $[a(2s + 2s) + b(2p\sigma + 2p\sigma), \sigma_g]$, where $a$ and $b$ are not known exactly, but $a > b$.

For the heteropolar molecules, we again have systematic symbols $(\sigma, \pi, \cdots)$ and informal symbols. Here relations are less symmetrical and more involved than in homopolar molecules. A form such as $(\sigma_O - s_C \pm \sigma_C)$ is intended to mean a molecular orbital whose form could be approximated by taking some linear combination of $2p\sigma$ of oxygen, $2s$ and $2p\sigma$ of carbon. In such a molecular symbol the atomic symbol which is written first (here $2p\sigma_O$) is supposed to be most prominent in the linear combination. Similarly, in $(\pi_O + \pi_C, \pi)$ of CO, $2p\pi_O$ is supposed to have the greater weight, in this case probably by a factor of two or three.

As for the occurrence of simple *atomic* orbitals in heteropolar molecules, we find examples of these above in $2s_O$ of CO and in $n_X p\pi$ and $n_Y p\pi$ of XY in (5). It should be noted that in heteropolar molecules one can go by continuous steps from molecular to atomic orbitals. Really, $(2s_O)$ in CO must contain a *little* admixture of $(2s_C)$ and might be written $(2s_O + 2s_C)$, while $n_Y p\pi$ and $n_X p\pi$ of XY can be written $(n_Y p\pi + n_X p\pi)$ and $(n_X p\pi - n_Y p\pi)$ as in (5*a*). Since, however, the proportion of the second-named constituent is undoubtedly small in the cases mentioned, the use of pure atomic orbitals is sensible as giving a simple good approximation.

Molecular orbitals of types $(\alpha + \alpha)$ and $(\alpha + \beta)$, or $(\alpha - \alpha)$ and $(\alpha - \beta)$, are, respectively, bonding or anti-bonding. Polar forces also enter, in the cases of heteropolar molecules. The effect of atomic orbitals is non-bonding, i.e., neutral.

## 2. Molecular and atomic ionization potentials

The *vertical ionization potentials* (cf. immediately following (6)) of molecules may be expected to behave as follows:[5] non-bonding orbitals, roughly the same potential as for the atom alone; bonding orbitals, larger ionization potential than for the atomic orbitals in terms of which they may be approximated, e.g. $(\pi + \pi, \pi_u)$ larger than $np\pi$ in (1)–(6) above; anti-bonding orbitals, lower potential than the related atomic orbitals.

The basis for these rules is fairly obvious. Non-bonding orbitals are affected only indirectly by the entrance of an atom into a molecule, although these indirect effects may sometimes be very appreciable for non-bonding electrons in the outer shell of an atom (cf. $np\pi$ of the HX molecules, Table I). Bonding molecular orbitals are of a type which must differ from corresponding atomic orbitals in such a way as to stabilize the resulting molecule, making its energy lower than that of the separate atoms. This can hardly be the case in homopolar or nearly homopolar molecules unless the electrons which occupy them (bonding electrons) have a considerably higher ionization potential than the corresponding electrons in the atoms before union. Similarly, anti-bonding molecular orbitals are by definition of such a nature than their occupation by electrons tends to cause the molecule to fall apart; they may have lower ionization potentials than the corresponding atomic orbitals. A well-known example is that of the $(\pi - \pi)$ orbital of NO, whose ionization potential is much less than that of any orbital of unexcited N or O. The preceding considerations have often been used in earlier papers. They will, however, now be made more precise.

In applying the foregoing rules, we should not in general compare the observed molecular ionization potential directly with the ordinary minimum ionization potential of the atom. In the first place, the vertical molecular ionization potential may need correction: (*a*) the energy of the neutral molecule may need to be corrected, if the given molecular electron configuration yields more than one state (example, $O_2$); for most molecules, however (closed-shell $^1\Sigma^+$ states), there is no such correction; (*b*) the energy of the positive molecule-ion may similarly need correction; e.g., in the $^2\Pi$ ions of the halogen

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[5] Cf. also the relations between atomic and molecular ionization potentials discussed by J. Savard, J. de Phys. et le Rad. [VII] **4**, 650 (1933); **5**, 27 (1934).

molecules, one should take the average energy of $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$.

More notable, the atomic ionization potential nearly always needs correction; the proper potential is one corresponding to the removal of an electron from a "*valence state*" of the *atom*,[6] of valence, say, $V_n$, giving a valence state of the *positive ion* of valence $V_{n+1}$ or $V_{n-1}$. Tables of such valence state ionization potentials of atoms are given in another paper.[6] An atomic valence state $V_n$ is appropriate when an atom uses $n$ valence electrons in forming the molecule; in the atom's valence state $V_n$, these are unpaired.

Removal of a non-bonding electron from the molecule corresponds to removing a non-valence electron from one atom, thus leaving an additional unpaired electron in the atom-ion; in the neutral atom, this was paired with the electron now removed. Thus there are $n+1$ unpaired electrons in the atom-ion, and one sees on due consideration that the proper atomic ionization potential is one corresponding to formation of an ion in a valence state $V_{n+1}$.[6] The corresponding valence ionization potential will be designated $I^*$ (cf. (4), (5) and (4*a*) above).

Removal of a bonding electron from a molecule usually corresponds to removal of one of the valence electrons from the atom; hence for an atom in a valence state $V_n$, the atom-ion should be taken in a valence state $V_{n-1}$. Such an ionization potential will here be designated $I^\circ$ (cf. (4), (5) and (4*a*)). In some cases, e.g., a $p^3$, $V_3$ atom, as N in $N_2$, $I^\circ$ is somewhat different for $p\pi$ than for $p\sigma$ (cf. Ref. 6, Table II).

When electrons in bonding orbitals of type $(a+a)$ are accompanied by anti-bonding electrons of type $(a-a)$, the situation is more or less altered, however. In case there is a complete shell of both of the molecular orbital types $(a+a)$ and $(a-a)$, as e.g., $(s+s)^2(s-s)^2$ in (1) above, or $(\pi+\pi)^4(\pi-\pi)^4$ in (4*a*), we should always consider the alternative mode of description using two closed shells of non-bonding atomic orbitals, as, e.g., $(2s)^2(2s)^2$ instead of $(s+s)^2(s-s)^2$ in (1), or $(np\pi)^4(np\pi)^4$ as in (4) instead of (4*a*). The second mode of description shows clearly that the proper comparison atomic ionization potential in such a case is of the type $I^*$, and this applies to both the bonding and the anti-bonding molecular orbitals, if we use these for the electron configuration (example, cf. (4*a*)).

In a case like that of $O_2$ (cf. (3) above), where bonding electrons of type $(a+a)$ are accompanied by a lesser number of anti-bonding electrons of type $(a-a)$, the situation is more complicated. Here there are several ways of ionizing the molecule, corresponding part to $I^*$ and part to $I^\circ$ of the atom. In cases like $(\sigma+\sigma)$ and $(\pi+\pi)$ of $N_2$ and $(\sigma+\sigma)$ of $X_2$, however, where anti-bonding electrons $(\sigma-\sigma)$ and $(\pi-\pi)$ are lacking, the proper atomic comparison potential is definitely $I^\circ$.

The observed vertical ionization potentials of diatomic molecules (either directly observed or obtained by correcting observed non-vertical,—adiabatic,—potentials to verticality) are in good accord with the rules stated above. For $N_2$, the comparison is given in (1) above; for $Cl_2$, $Br_2$, and $I_2$, in Table I.

For heteropolar molecules, comparisons are often more difficult, since one often has orbitals intermediate between bonding and non-bonding, and other complications. For the $(\pi_O+\pi_C)$ orbital of CO, for example, we should expect $I > \frac{1}{2}(I^\circ{}_O + I^\circ{}_C)$ if $\pi_O$ and $\pi_C$ were equally represented in $(\pi_O+\pi_C)$, but $I = I^*{}_O$ for pure $\pi_O$. The actual case is believed to be intermediate. Now $\frac{1}{2}(I^\circ{}_O + I^\circ{}_C)$ is about 14 volts, while $I^*{}_O$ is 14.73 volts.[6] The observed $I=17.1$ volts is reasonably consistent with our expectations. Similarly for the CO orbital called $(s_C+\sigma_O)$, we expect $I>\{\frac{1}{2}[I^*{}_C(s)+I^*{}_O(p)]=16.8\}$ for equal representation of $s_C$ and $\sigma_O$, and $I=I^*{}_C(s)=18.8$ volts for pure $s_C$; the observed is 19.7 volts. An added complication in some cases (*e.g.*, $N_2$, CO) is $s-p$ hybridization.

In most of the molecules HX and XY the binding is more nearly homopolar than heteropolar. A good atomic comparison potential for the $\sigma$ bonding orbital in such molecules appears to be $\frac{1}{2}(I^\circ{}_X+I_H)$ or $\frac{1}{2}(I^\circ{}_Y+I^\circ{}_X)$; this becomes $I^\circ{}_X$, as it should, for X=Y. The same simple comparison potential may perhaps be best even for more heteropolar molecules, since otherwise we have various complications, e.g., if we give extra weight to the $I$ of the more negative atom, we ought perhaps to take the latter as a negative

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[6] Cf. paper by R. S. Mulliken on electronegativities, Section C and Table IV; to appear in J. Chem. Phys., Oct. or Nov., 1934.

TABLE I. *Vertical ionization and excitation potentials I and E (volts)*[a].

| *Ionization Process* | *Molecule* | *Predicted* $I^b$ | *Obs.* $I^{c,\,d}$ |
|---|---|---|---|
| HX : $\sigma^2\pi^4$, $^1\Sigma^+ \rightarrow \sigma^2\pi^3$, $^2\Pi$, corresponding to<br>X : $p^5, V_1 \rightarrow p^4, V_2 : I^*_X$ | HF | 18.23 | —— |
| | HCl | 13.66 | 13.75 +0.04 |
| | HBr | 12.43 | 13.25 +(0.16) |
| | HI | 11.16 | 12.75 +(0.33) |
| HX : $\sigma^2\pi^4 \rightarrow \sigma\pi^4$, $^2\Sigma^+$, corresponding to X : $p^5, V_1 \rightarrow p^4, V_0 : I^\circ_X$<br>or to H(1$s$, $V_1$)→$H^+$, $V_0$ : $I_H$.<br>Predicted $I$ from ave. of $I^\circ_X$ and $I_H$. | HF | >17.35 | —— |
| | HCl | >14.69 | 17.45 |
| | HBr | >13.99 | —— |
| | HI | >13.23 | —— |
| XY : $\sigma^2\pi_Y{}^4\pi_X{}^4$, $^1\Sigma^+ \rightarrow \sigma^2\pi_Y{}^4\pi_X{}^3$, $^2\Pi$, corresponding to<br>X : $p^5$, $V_1 \rightarrow p^4$, $V_2 : I^*_X$ | BrCl | 12.43 ($\pi_{Br}$) | —— |
| | | 13.66 ($\pi_{Cl}$) | —— |
| | IBr | 11.16 ($\pi_I$) | —— |
| | | 12.43 ($\pi_{Br}$) | —— |
| XY : $\sigma^2\pi^4\pi^4 \rightarrow \sigma^2\pi_Y{}^3\pi_X{}^4$, $^2\Pi$<br>Y : $p^5$, $V_1 \rightarrow p^4$, $V_2 : I^*_Y$ | ICl | 11.16 ($\pi_I$) | —— |
| | | 13.66 ($\pi_{Cl}$) | —— |
| XY : $\sigma^2\pi^4\pi^4 \rightarrow \sigma\pi^4\pi^4$, $^2\Sigma^+$, corresponding to<br>Y or X : $p^5$, $V_1 \rightarrow p^4$, $V_0$ : $I^\circ_Y$ or $I^\circ_X$<br>Predicted $I$ from ave. of $I^\circ_Y$ and $I^\circ_X$. | BrCl | >15.14 | —— |
| | IBr | >13.68 | —— |
| | ICl | >14.38 | —— |
| $X_2$ : $\sigma^2\pi^4\pi^4$, $^1\Sigma^+{}_g \rightarrow \sigma^2\pi^4\pi^3$, $^2\Pi_{g,\,u}$, corresponding to<br>X : $p^5$, $V_1 \rightarrow p^4$, $V_2 : I^*_X$ | $F_2$ | 18.23(*ave.* $^2\Pi_g$, $^2\Pi_u$) | —— |
| | $Cl_2$ | 13.66 " | 13.2(+0.04) : $^2\Pi_g$ |
| | $Br_2$ | 12.43 " | 12.8(+0.16) : $^2\Pi_g$ |
| | $I_2$ | 11.16 " | 10.0(+0.33) : $^2\Pi_g$ |
| $X_2$ : $\sigma^2\pi^4\pi^4 \rightarrow \sigma\pi^4\pi^4$, $^2\Sigma^+{}_g$, corresponding to<br>X : $p^5$, $V_1 \rightarrow p^4$, $V_0$ : $I^\circ_X$ | $F_2$ | >21.17 | —— |
| | $Cl_2$ | >15.84 | —— |
| | $Br_2$ | >14.44 | —— |
| | $I_2$ | >12.93 | (14.2?)[f] |
| *Excitation Process* | *Molecule* | *Obs.* $E^e$ | *Term Value*[f] |
| XY or $X_2$ : $\sigma^2\pi^4\pi^4 \rightarrow \sigma^2\pi^4\pi^3\sigma^*$, $\Pi_{1,\,0,\,1,\,2}$ (mean) (cf. section 7) | BrCl | 3.17 | (9.3) = $\sigma^*$ |
| | IBr | 2.25 | (8.9) |
| | ICl | 2.41 | (8.8) |
| | $F_2$ | 4.24 | (14.0) |
| | $Cl_2$ | 3.7 | 9.5 |
| | $Br_2$ | 2.88 | 10.1 |
| | $I_2$ | 2.10 | 8.2 |
| Same, except $\sigma^\times$ (cf. section 6) | BrCl | 7.46 | (4.97) = $\sigma^\times$ |
| | IBr | 6.67 | (4.49) |
| | ICl | 6.90 | (4.26) |
| | $I_2$ | (7.4) | (2.9) |
| XY or $X_2$ : $\sigma^2\pi^4\pi^4 \rightarrow \sigma\pi^4\pi^4\sigma^*$, $^{1,3}\Sigma^+$ (mean) (cf. section 9) | $I_2$ | (6.1) | (14.3) = $\sigma$ |
| | ICl | [8.0][f] ⟵ | [16.8] = $\sigma$ |

*Notes for Table I:* (**a**) A "vertical" ionization potential corresponds to a process in which ionization is accomplished without change in the distance between nuclei. (**b**) Cf. section 2 of text; and reference 6 for numerical data on $I^*$ and $I^\circ$. The predicted $I$ values here refer, in the case that the molecular ion is in a $^2\Pi$ state, to the mean of the $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$ substates. (**c**) Directly observed $I$ values for production of $^2\Pi$ molecular ions of course belong to $^2\Pi_{1\frac{1}{2}}$; following each directly observed $I$ is the correction needed (*estimated*, if in parentheses) to bring it up to the mean $(^2\Pi_{1\frac{1}{2}} + {}^2\Pi_{\frac{1}{2}})/2$ and thus make it comparable with the predicted $I$; for example, in the case of HBr, the observed $I$ is 13.25, the estimated correction 0.16. Corrections for lack of verticality of observed $I$'s have not been made (because probably negligible compared with the error of measuring $I$) except in the case of the $\sigma$ ionization potential of HCl (17.45 volts), where the correction (0.33 volts) has been included. In the cases of $Cl_2$, $Br_2$ and $I_2$, it should be noted that the observed potentials doubtless correspond to production of a $^2\Pi_g$ ion, and should for this reason be less than the predicted values, which refer to the average of $^2\Pi_g$ and $^2\Pi_u$. (**d**) The observed $I$ values for $\pi$ ionization of HX are averages of closely agreeing electron impact values by Knipping (Zeits. f. Physik **7**, 328 (1931)), and Mackay (Phys. Rev. **24**, 319 (1924)); it should be noted that Mackay's $I$ measurements have in nearly all cases proved unusually reliable. The $I$ values for $X_2$ are also by Mackay; also note that Mohler and Foote get 10.1 volts for $I_2$ (Phys. Rev. **21**, 382 (1923)), while Hogness and Harkness (Phys. Rev. **32**, 784

(1928)) get evidence that the $I_2$ ionization potential is less than that of the I atom. The $\sigma$ potential for HCl is from the $I=13.75$ for HCl, combined with spectroscopic data on $HCl^+$. (e) For $\pi\rightarrow\sigma^*$ the mean excitation potentials $E$ are based on the observed maximum ($\lambda_{max}$, cf. Table IIB) of continuous absorption (process $^3\Pi_{0+}\leftarrow{}^1\Sigma^+$), minus an estimated correction to reduce this to the desired value, i.e., to the mean $E$ for $^3\Pi_1$ and $^1\Pi$ of $\sigma^2\pi^4\pi^3\sigma^*$. For $\pi\rightarrow\sigma^\times$, the $E$ values for XY are accurate, from data of Cordes and Sponer;[9] the value for $I_2$ assumes the λ1750 bands[10] to be analogous to the longer-wave $\pi\rightarrow\sigma^\times$ bands of XY. For $\sigma\rightarrow\sigma^*$, we have only the approximate vertical $E=6.5$ volts for $\cdots\sigma^*$, $^1\Sigma^+_u$ of $I_2$ (cf. reference 13). The mean $E$ of $^1\Sigma^+$ and $^3\Sigma^+$ is here estimated as 6.1 volts. (f) The values for $\sigma^*$ and $\sigma^\times$ were obtained by subtracting $E$ values from $\pi_X$ $I$ values. Corrected experimental $I$ values were used for $X_2$ ($^2\Pi_g$, mean, *viz.*, 13.2, 13.0, 10.3 for $Cl_2$, $Br_2$, $I_2$), predicted values for XY. The $\sigma^\times$ term values thus obtained for XY appear to be too large, which indicates that the predicted $I$ values for XY are too large (cf. section 6). The term value for $\sigma$ of $I_2$ is obtained by adding $(6.1)=(\sigma\rightarrow\sigma^*)$ to the term value 8.2 of $\sigma^*$ as obtained above. The $E$ for ICl is based on an estimated $\sigma$ and semi-observed $\sigma^*$ term value.

ion, in the field of a positive ion. Such considerations would affect somewhat the discussion of CO above, but the existence of multiple bonding there can allow some orbitals to be one-sided without making the molecule as a whole polar.

In the cases of HCl, HBr, HI (cf. Table I), the observed (probably nearly vertical) and predicted ionization potentials agree well for HCl, but in going from HCl to HI, the observed $\pi$ potentials do not decrease as fast as expected. The non-bonding $np\pi$ electrons are unexpectedly difficult to ionize. Possibly the $np\pi$ orbitals have appreciable bonding power in HI, containing an appreciable contribution from $2p\pi$ of H. On the other hand, the strong tendency toward $H^+Cl^-$ character in HCl might be expected to lessen the ionization potential of $3p\pi$ there, because of the shielding effect of the extra Cl electron.

## II. The Halogen Molecules and Their Spectra

### 3. Halogen ions XY+

We turn now to a more detailed consideration of the halogens. Having described the normal states in (4) and (5), we may consider next the low-energy states of the ions $X_2^+$ and $(XY)^+$, as a step toward understanding excited states of the neutral halogens. Taking ICl as an example of the XY type, the lowest-energy state of $(ICl)^+$ should be obtained by removing one iodine $5p\pi$ electron from (5), leaving

$$I^+Cl: \quad \cdots(3p\sigma_{Cl}+5p\sigma_I,\ \sigma)^2(3p\pi_{Cl})^4(5p\pi_I)^3,\ {}^2\Pi_{1\frac{1}{2},\ \frac{1}{2}}. \tag{7}$$

The $^2\Pi$ should be inverted, with a doublet interval roughly equal to the spin-orbit coupling coefficient $a$ of an $I^+$ atom,[7] since it is determined by the group $(5p\pi)^3$ of $I^+$ (but see end of next paragraph). Although $a$ is not known for $I^+$ (or $Br^+$), it can be estimated using the fact that $a$ for the normal state of $F^+$ is 21 percent larger than for that of F, and for $Cl^+$ 13 percent larger than for Cl. We may estimate $a$ for $I^+$ as about 10 percent greater than for I, where $a=(\frac{2}{3})(^2P_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}})=(\frac{2}{3})(0.94)$ volts; this gives $a=0.69$ volts as the estimated width of $^2\Pi$ for $I^+Cl$ in (7). Of course one does not expect to find exactly this value, since the $5p\pi$ orbitals of $I^+$ are appreciably affected by the presence of the ICl bond (cf. next paragraph), and by a tendency toward validity of (5*a*), which would cause some mixing in of $3p\pi$ of Cl and a consequent lowering of $a$. Evidence supporting these predictions as to $ICl^+$ is found in the interpretation of the vacuum ultraviolet spectrum of ICl given in section 6.

Since Cl is more electronegative than I, the neutral molecule ICl is expected to show polarity corresponding to a partial realization of the formulation $I^+Cl^-$; this is expressed in (5) in the fact that in the bonding orbital $(3p\sigma_{Cl}+5p\sigma_I)$, the $3p\sigma_{Cl}$ constituent predominates. In the normal state of $(ICl)^+$, the $5p\pi$ ionization of the I atom should tend to attract electrons toward the latter, and so probably strongly reverse the polarity of the I—Cl bond, making it $(\sigma_I+\sigma_{Cl},\ \sigma)^2$. Hence, although the ionization is primarily in the I atom, so that the normal state of the molecule may be fairly well characterized as $I^+Cl$, nevertheless the ionization must be partly at the expense of the Cl. A consequence of this is that the estimate of the width of the $^2\Pi$ of (7), given above as somewhat less than $a$ of $I^+$, should be somewhat further reduced. An additional complication which may affect the $^2\Pi$ width is the existence of a marked tendency toward case $c$ (atom-like) coupling,[1] which would allow only Ω, but not Λ and $S$, to be good quantum numbers.

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[7] Cf. R. S. Mulliken, Rev. Mod. Phys. **4**, 34–39 (1932).

On dissociation, both components of the ${}^2\Pi$ of (7) should give $I^+({}^3P_2) + Cl({}^2P_{1\frac{1}{2}})$, as can be shown from the usual rules.[1] The energy of dissociation $D$ could be calculated exactly from the known $D$ of ICl (2.14 volts to give I, ${}^2P_{1\frac{1}{2}}$ + Cl, ${}^2P_{1\frac{1}{2}}$), if we knew the $I$ value for ICl to give ${}^2\Pi_{1\frac{1}{2}}$ of $I^+Cl$ and of the I atom to give $I^+({}^3P_2)$. The predicted approximate value of the former (cf. Table I), and the estimated value of the latter,[6] are, respectively, $(11.16-0.33=)$ 10.83, and 10.55, volts. Supposing these correct, $D$ of $I^+Cl$ would be 1.87 volts and 1.18 volts for the ${}^2\Pi_{1\frac{1}{2}}$ and the ${}^2\Pi_{\frac{1}{2}}$ levels, respectively. The values of $r_e$ for these levels would probably not differ radically from that of neutral ICl, since the $(\sigma_{Cl}+\sigma_I)^2$ bond in $I^+Cl$ is not radically different from that in ICl.

If we denote the electron configuration of the normal state of $(ICl)^+$ briefly by $\sigma^2\pi^4\pi^3$ (cf. (7)), the existence of many excited states of fairly low energy, with configurations $\sigma^2\pi^3\pi^4$, $\sigma\pi^4\pi^4$, $\sigma^2\pi^4\pi^2\sigma^*$, $\sigma^2\pi^3\pi^3\sigma^*$, etc., can be predicted, where $\sigma^*$ is of the anti-bonding type $(5p\sigma_I-3p\sigma_{Cl})$. Of these probably most are repulsive states, i.e., states with no minimum or practically none in their $U(r)$ curves.

For example, the inverted ${}^2\Pi$ state $\sigma^2\pi^3\pi^4$, obtainable by removing a $3p\pi$ Cl electron from (5), should be about 2.8 volts above the ${}^2\Pi_{1\frac{1}{2}}$ normal state of $(ICl)^+$, according to Table I. [$I=11.16$ volts predicted for production of $\sigma^2\pi^4\pi^3$, ${}^2\Pi$ (mean), 13.66 volts for $\sigma^2\pi^3\pi^4$, ${}^2\Pi$ (mean); or 10.82 and 13.62, for ${}^2\Pi_{1\frac{1}{2}}$ ions. This, of course, refers to vertical processes of ionization.] The separation ${}^2\Pi_{\frac{1}{2}}-{}^2\Pi_{1\frac{1}{2}}$ in this state should be about equal to $a$ of $Cl^+$, or 0.08 volt.[7] If this state on dissociation gives ${}^3P_2$ of $I^+$ plus ${}^2P_{1\frac{1}{2}}$ of Cl, as is theoretically possible, then it should probably be unstable, since the energy 2.8 volts required for its vertical excitation considerably exceeds the estimated $D$ of unexcited ICl. If, however, the $U(r)$ has a minimum, this should probably be at an $r_e$ value not radically different from that of unexcited $(ICl)^+$ and ICl, since the $(\sigma+\sigma)^2$ bond still remains.

A third state of considerable interest, although in all probability repulsive, is $\sigma\pi^4\pi^4$, ${}^2\Sigma^+$. The vertical excitation potential for this should be in excess of 5 volts, according to Table I (probably as much as 6 volts). Certain other excited states of lower energy, besides the ${}^2\Pi$ above discussed, should, however, exist. According to Table I, only about 2.3 volts is required for the vertical excitation process $\sigma^2\pi^4\pi^4$, ${}^1\Sigma^+\rightarrow\sigma^2\pi^4\pi^3\sigma^*$, ${}^{1,3}\Pi$ (mean) in neutral ICl. Hence in $(ICl)^+$ the group of states belonging to $\sigma^2\pi^4\pi^2\sigma^*$ may be expected to be about 2.3 volts above $\sigma^2\pi^4\pi^3$, ${}^2\Pi$ (mean). The states of $\sigma^2\pi^3\pi^3\sigma^*$ should come near 5.1 volts.

No bands attributed to $(ICl)^+$ are yet known, but according to the foregoing it is possible that visible bands may exist, corresponding to transitions from states of $\sigma^2\pi^4\pi^3$ or $\sigma^2\pi^4\pi^2\sigma^*$ to the normal state. It may be, however, that the excited states mentioned are all unstable and can give no emission bands.

Two of the excited states of $(ICl)^+$ just mentioned may be written as:

$$\left.\begin{array}{ll}(ICl)^+: & \\ \cdots(3p\sigma+5p\sigma,\,\sigma)^2(3p\pi_{Cl})^3(5p\pi_I)^4,\ {}^2\Pi_{1\frac{1}{2},\,\frac{1}{2}}, & \\ \text{and} \qquad \cdots(\sigma+\sigma)(\pi_{Cl})^4(\pi_I)^4,\ {}^2\Sigma^+ & \end{array}\right\}. \qquad (8)$$

## 4. Halogen ions $X_2^+$

Halogen ions of the types $(XY)^+$ and $X_2^+$ should differ considerably in some respects. Taking $I_2$ as an example, we find that three low-energy states of $I_2^+$ analogous to the states (7) and (8) of $(ICl)^+$ can be obtained by removal of one electron. They are:

$$\cdots(5p\sigma+5p\sigma,\,\sigma_g)^2(5p\pi)^4(5p\pi)^3,\ {}^2\Pi_{g1\frac{1}{2},\,\frac{1}{2}}, \qquad (9)$$

$$\cdots(\qquad\qquad\qquad)^2(\qquad)^4(\qquad)^3,\ {}^2\Pi_{u1\frac{1}{2},\,\frac{1}{2}}, \qquad (10)$$

$$\cdots(\qquad\qquad\qquad)(\qquad)^4(\qquad)^4,\ {}^2\Sigma^+{}_g. \qquad (11)$$

Starting from the formulation (4) for $I_2$, one might at first expect for $I_2^+$ to find two ${}^2\Pi$ states, $\cdots(5p\pi)^4(5p\pi)^3$ and $\cdots(5p\pi)^3(5p\pi)^4$, with equal energy. Actually, however, the vacancy in the $(5p\pi)^4$ shell jumps back and forth between the two atoms with considerable speed, so that the formulation $(5p\pi)^{3\frac{1}{2}}(5p\pi)^{3\frac{1}{2}}$ might give a better description. This exchange of the vacancy corresponds to a quantum-mechanical resonance between $\pi^4\pi^3$ and $\pi^3\pi^4$, and we get two states, ${}^2\Pi_g$ and ${}^2\Pi_u$, both of type $\pi^{3\frac{1}{2}}\pi^{3\frac{1}{2}}$, although for systematic reasons we use the designation $\pi^4\pi^3$ for both (cf. (9) and (10)). Both should be inverted and each should have a doublet separation about equal to $a$ of the $I^+$ or I atom, i.e., about 0.7 volts (cf. discussion of $I^+Cl$ in section

3). The energy difference between the $^2\Pi_g$ and the $^2\Pi_u$ should probably not be large, since the atomic groups $(5p\pi)^4$ and $(5p\pi)^3$ are far apart and do not overlap much. Possibly the interaction is so small that the doublets overlap, giving the energy order $^2\Pi_{1\frac{1}{2}g}$, $^2\Pi_{1\frac{1}{2}u}$, $^2\Pi_{\frac{1}{2}g}$, $^2\Pi_{\frac{1}{2}u}$.

That the $^2\Pi_g$ is the lower can be readily seen by using molecular orbitals for the $5p\pi$ electrons (cf. 4*a*). Then, to get the actual case, we interpolate between the case using molecular orbitals and the other ideal case (4), in which we have precisely zero interaction so that $^2\Pi_g$ and $^2\Pi_u$ are equal in energy. Starting from $\sigma_g{}^2\pi_u{}^4\pi_g{}^4$ as in (4*a*), one can remove either one $\pi_g$ to get $^2\Pi_g$, or one $\pi_u$ to get $^2\Pi_u$. Since $\pi_g$ is the more easily ionized, $^2\Pi_g$ is the lower in energy.

The two low $^2\Pi$ levels should probably have about the same $r_e$ as neutral $I_2$, since the bond $(\sigma_g{}^2)$ remains unchanged. If the two levels differ much in energy, however, the lower one should have somewhat the smaller, the upper one somewhat the larger, $r_e$.

The observed ionization potentials of $Cl_2$, $Br_2$, $I_2$ (cf. Table I) are on the whole somewhat lower than the values predicted on the assumption that the $np\pi$ electrons are non-bonding; this is what would be expected if the $^2\Pi_u$ and $^2\Pi_g$ states of $X_2^+$ differ appreciably in energy, the former being then produced at a lower ionization potential than if their energies were equal.

Both of the low $^2\Pi$ states of $I_2^+$ should give unexcited $I + I^+$ on dissociation $(^2P_{1\frac{1}{2}} + {}^3P_2)$. If $I$ values were known accurately for I and for $I_2$, and the $^2\Pi_u$, $^2\Pi_g$ separation in $I_2^+$ were known, the $D$ values of these states could be calculated from the known $D$ of $I_2$. On the basis of the considerations given above and the data in Table I, it seems likely that the $D$'s of the $^2\Pi_{1\frac{1}{2}u}$ and $^2\Pi_{\frac{1}{2}u}$ are of the same order of magnitude as for neutral $I_2$, while those of the $^2\Pi_g$ are less but still large enough to give stability.

More than two volts, probably about 4 volts, measured vertically (cf. Table I), above the $^2\Pi_g$ normal state of $I_2^+$ should come the $\sigma_g\pi^4\pi^4$, $^2\Sigma^+{}_g$ state. This state, which should give $^2P_{1\frac{1}{2}} + {}^3P_2$ (or $^3P_1$) on dissociation, is very likely of the repulsive type. Other low-energy states of $I_2^+$, some of which may be stable, should exist with the configuration $\sigma_g{}^2 5p\pi^3 5p\pi^3(5p\sigma - 5p\sigma,\ \sigma_u)$; this should give nine electronic states.

Visible $I_2^+$ bands corresponding to transitions connecting some of the excited states mentioned with the ground state may exist, but have not yet been definitely found. Certain emission bands of $I_2$, $Br_2$ and $Cl_2$ may, however, prove to be due to $I_2^+$, $Br_2^+$ and $Cl_2^+$, although further work on them is needed.[8] The analyses of these bands are incomplete, but in the case of $Br_2$ there appear to be two systems with a common lower state having $\omega_e'' = 362$; the upper levels have $\omega_e'$ about 193 and 153. If these bands are really $Br_2^+$, the $\omega_e''$ value 362 is reasonable for the $^2\Pi_g$ (normal) state of the latter. For neutral $Br_2$, $\omega_e$ is 324. The somewhat higher value for $Br_2^+$ would indicate that the strength of the bond is somewhat increased by the net action of the seven $\pi$ electrons, corresponding to an appreciable tendency from (4) toward (4*a*).

## 5. Excited states of halogens XY and $X_2$

The excited states of ICl and $I_2$ (examples of XY and $X_2$) may be thought of as obtained by adding one electron in an "*excited orbital*" to any of the various states of the ions $(ICl)^+$ and $I_2^+$. Each excited orbital has an ionization potential (term value) which is smaller than that of any unexcited orbital, i.e., orbital present in the unexcited molecule. Most of the excited orbitals are related to *excited atomic* orbitals and should have term values not over 3 or 4 volts. There is, however, one excited orbital with an ionization potential of the same order of magnitude as the ordinary ionization potential of the molecule. This is the important anti-bonding $\sigma$ orbital $(5p\sigma_{\mathrm{I}} - 3p\sigma_{\mathrm{Cl}},\ \sigma)$ of ICl or $(5p\sigma - 5p\sigma,\ \sigma_u)$ of $I_2$, complementary to the bonding orbital $(3p\sigma_{\mathrm{Cl}} + 5p\sigma_{\mathrm{I}})$ or $(5p\sigma + 5p\sigma,\ \sigma_g)$. It will be convenient to call this $\sigma^*$ or $\sigma^*{}_u$.

The lowest excited states of ICl or $I_2$ are obtained by adding $\sigma^*$ to the normal state (7) or (9) of $(ICl)^+$ or $I_2^+$:[1]

$$\mathrm{ICl}\colon\ \sigma^2\pi_{\mathrm{Cl}}{}^4\pi_{\mathrm{I}}{}^3\sigma^*,\ {}^{1,3}\Pi;\quad \mathrm{I}_2\colon\ \sigma_g{}^2\pi^4\pi^3\sigma^*{}_u,\ {}^{1,3}\Pi_u. \qquad (12)$$

Transitions from the normal state of ICl or $I_2$ (cf. (4) and (5)) to the $^3\Pi_{0+}$ and $^3\Pi_1$ levels of (12) give the well-known visible and infrared

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[8] $Br_2$ and $Cl_2$: Y. Uchida and Y. Ota, Jap. J. Phys. **5**, 53, 59 (1928); $I_2$ (weak group near λ2700): G. Cario and O. Oldenberg, Zeits. f. Physik **31**, 914 (1925); also the visible Geissler tube emission spectra of $I_2$ may perhaps be in part $I_2^+$ bands.

absorption bands of ICl and $I_2$; analogous statements apply for XY and $X_2$.[1]

Above the $^{1,3}\Pi$ of ICl given by (12) there should be another $^{1,3}\Pi$; and a little above the $^{1,3}\Pi_u$ of $I_2$ there should be a $^{1,3}\Pi_g$:

$$\text{ICl: } \sigma^2\pi_{\text{Cl}}{}^3\pi_{\text{I}}{}^4\sigma^*, {}^{1,3}\Pi; \quad \text{I}_2\text{: } \sigma_g{}^2\pi^4\pi^3\sigma^*{}_u, {}^{1,3}\Pi_g. \tag{13}$$

These states are those obtained by adding $\sigma^*$ to the low $^2\Pi$ excited state of $(\text{ICl})^+$,—cf. (8),—or $\sigma^*{}_u$ to the low $^2\Pi_u$ of $I_2{}^+$. The center of gravity of the $^{1,3}\Pi$ of (13) for ICl should then be about 2.5 volts above that of (12), this interval being that between the two $^2\Pi$'s in $(\text{ICl})^+$, as estimated in Table I. The interval from $^{1,3}\Pi_u$ of (12) to $^{1,3}\Pi_g$ of (13) for $I_2$ is probably less than 1 volt, like the estimated interval between the low $^2\Pi_g$ and $^2\Pi_u$ of $I_2{}^+$ (cf. section 4).

Still higher in energy should be the states obtained by adding $\sigma^*$ to the $^2\Sigma^+$ of (8) or (11);

$$\text{ICl: } \sigma\pi^4\pi^4\sigma^*, {}^{1,3}\Sigma^+; \quad \text{I}_2\text{: } \sigma_g\pi^4\pi^4\sigma^*{}_u, {}^{1,3}\Sigma^+{}_u. \tag{14}$$

Transitions to these states from the normal state should occur in the cases of both ICl and $I_2$. These, as well as transitions involving the states of (12) and (13), will be fully discussed in sections 9–10 below.

Numerous additional excited states (cf. Tables III, IV) are obtainable by adding a $\sigma^*$ electron to one of the following several states of $(\text{ICl})^+$ or corresponding $I_2{}^+$ states: $\sigma^2\pi^4\pi^2\sigma^*$, $\sigma^2\pi^3\pi^3\sigma^*$, $\sigma^2\pi^2\pi^4\sigma^*$, $\sigma\pi^4\pi^3\sigma^*$, $\sigma\pi^3\pi^4\sigma^*$, $\pi^4\pi^4\sigma^*$.

Infinitely many additional excited states are obtainable by adding an electron in an excited orbital other than $\sigma^*$ to any of the states of $(\text{ICl})^+$ or $I_2{}^+$. We shall consider only the lowest-energy excited states of this category, namely, those obtainable by using the normal $^2\Pi$ state of $\text{ICl}^+$, or the normal $^2\Pi_g$ or low-energy $^2\Pi_u$ of $I_2{}^+$, and adding an electron in the most firmly bound type of excited orbital other than $\sigma^*$.

All of the outer-electron orbitals involved in (4)–(5) and (7)–(14) are, or correspond on dissociation to, unexcited halogen atom orbitals, and have ionization potentials of the order of 10 volts or more. The stages of excitation with which we are now concerned, however, involve an excited orbital one unit greater in principal quantum number in the halogen atom, and therefore much larger in size and with an ionization potential of only 3 or 4 volts.

For our purposes it is not necessary to inquire further into the exact nature of the next-most-firmly-bound-after-$\sigma^*$ orbital. It is sufficient that it is probably a $\sigma$ orbital of large size and weak bonding power. Let us call it $\sigma^\times$. We shall be especially interested in the states:

$$\left.\begin{array}{r} \text{XY: } \sigma^2\pi_{\text{Y}}{}^4\pi_{\text{X}}{}^3\sigma^\times, \Pi_{1,\,0,\,1,\,2} \\ \text{X}_2\text{: } \sigma_g{}^2\pi^4\pi^3\sigma^\times, \Pi_{(1,\,0,\,1,\,2)g,\,u} \end{array}\right\}. \tag{15}$$

## 6. $\Omega$–*s* (*J*–*J*-like) coupling in halogen molecules: vacuum ultraviolet bands

In the states (15), the coupling between the $\sigma^\times$ excited electron and the $XY^+$ or $X_2{}^+$ core should be weak. The situation should strongly resemble that in the excited states of the rare gas,—or halogen,—atoms; in other words, the coupling should be of a $J$–$J$-like type similar to that between *e.g.* the $3p^5$, $^2P_{1\frac{1}{2}}$ or $3p^5$, $^2P_{\frac{1}{2}}$ core of ionized argon and a $4s$ electron. Comparison with the rare gases indicates coupling practically completely of the $J$–$J$-like type for the states (15) of all halogen molecules except $F_2$ and perhaps ClF and $Cl_2$. Even in the states (12) and (13) a strong $J$–$J$ tendency would also be expected.

For $J$–$J$-like coupling, the $\Pi$ states in (15) would not be definitely either singlet or triplet, but would have the combining properties of both. They could most accurately be described as follows:

$$\text{XY: } \{[\sigma^2\pi_{\text{Y}}{}^4\pi_{\text{X}}{}^3, {}^2\Pi_{1\frac{1}{2}}]\sigma^{\text{x}}\}_{2,\,1} \quad \text{and}$$
$$\{[\sigma^2\pi_{\text{Y}}{}^4\pi_{\text{X}}{}^3, {}^2\Pi_{\frac{1}{2}}]\sigma^{\text{x}}\}_{0,\,1}, \tag{16}$$
$$\text{X}_2\text{: } \{[\sigma_g{}^2\pi^3\pi^4, {}^2\Pi_{u1\frac{1}{2}}]\sigma^{\text{x}}{}_g\}_{2,\,1\,u} \quad \text{and}$$
$$\{[\sigma_g{}^2\pi^3\pi^4, {}^2\Pi_{u\frac{1}{2}}]\sigma^{\text{x}}{}_g\}_{0,\,1\,u}. \tag{17}$$

In (16) and (17), we have a core with good quantum numbers $S_c$, $\Lambda_c$, $\Sigma_c$, $\Omega_c$. To the magnetic axis defined by $\Omega_c$ is weakly coupled the spin $s_{ex}$ of the $\sigma^{\text{x}}$ excited electron, with quantum number $\sigma_{ex} = \pm\frac{1}{2}$, giving a resulting $\Omega = \Omega_c \pm \frac{1}{2}$. In this type of coupling, which may be designated $\Omega$–$s$ coupling, the molecule as a whole has $\Lambda(=\Lambda_c)$ and $\Omega$ as good quantum numbers, but it has no quantum number $S$. [A more complicated type of coupling, in which $\Lambda$ might no longer be a good quantum number, would occur if the excited electron had $\lambda > 0$, e.g., if it were $\pi$ or $\delta$.

It may also be pointed out that $\Omega$–$s$ coupling depends on the existence of a strong $\Lambda_c$–$\Sigma_c$ coupling within the core, which is of course impossible unless $\Lambda > 0$.] Selection rules for a transition between two states both having $\Omega$–$s$ coupling may be summarized as follows: transitions within the core are the same as if the excited electron were absent ($\Delta\Lambda_c$, $\Delta\Omega_c = 0, \pm 1$ with $\Delta\Omega_c = \Delta\Lambda_c$), while $\Delta\Omega = 0, \pm 1$; in practice, because $\Omega$–$s$ coupling, which depends on strong spin-orbit coupling in the core, may be expected often to be modified by a marked tendency toward atomic spin-orbit (case $c$) coupling,[1] $\Lambda_c = \Lambda$ is likely to be not entirely well-defined, so that the rules $\Delta\Lambda = 0, \pm 1$ and $\Delta\Lambda = \Delta\Omega_c$ are not strict. Transitions from an ordinary (case $b$ or $a$) state to a state with $\Omega$–$s$ coupling should be limited only by $\Delta\Lambda = 0, \pm 1$, $\Delta\Omega = 0, \pm 1$, with no $\Delta\Omega = \Delta\Lambda$ restriction.

In the case of $X_2$ in (17), the $\sigma^x$ is assumed to be $\sigma^x{}_g$; this then requires a ${}^2\Pi_u$ core to give ${}_u$ total states. There would also be similar states of $X_2$, of lower energy, with ${}^2\Pi_g$ core, but the total states would then be ${}_g$, and transitions to them from the ${}^1\Sigma^+{}_g$ normal state of $X_2$ would be contrary to the $g \leftarrow\!\!\rightarrow u$ selection rule. That the lowest excited $\sigma^x$ orbital is $\sigma^x{}_g$ is indicated by analogy with the cases of $He_2$ and $H_2$ (cf. Ref. 7, pp. 59–64). In $He_2$, the lowest $\sigma^x$ is $2s\sigma_g$, which is weakly bonding and is much larger than the (${}^2\Sigma^+{}_u$) $He_2{}^+$ core, closely resembling a $2s$ united-atom orbital; the $2s\sigma_g$ in $He_2$ is the first of a Rydberg series of atom-like molecular orbitals. By analogy, the lowest excited $\sigma^x$ in $X_2$ is probably a weakly bonding type $(n+1)s\sigma_g$, where $n = 2, \cdots 5$ for F, $\cdots$I. Following the analogy to $He_2$, the next $\sigma^x$ orbitals should be $(n+1\,?)p\sigma_u$, $(n+1)p\pi_u$, $(n+1)d\sigma_g$, etc. It seems likely that the ${}^2\Pi_u$ core plus $(n+1)s\sigma_g$ is lower in energy than ${}^2\Pi_g$ plus $p\sigma_u$. The nature of the $\sigma^x$ orbitals in the XY type is more difficult to predict, but presumably they are large and atom-like, at any rate.

In (16), if the coupling of $\sigma^x$ to the $(XY)^+$ core is very weak, the two components $\Omega = 0$ and 1 derived from ${}^2\Pi_{\frac{1}{2}}$ of $(XY)^+$ by the coupling of $\Omega$ of the core with $s$ of $\sigma^x$, should be close together, and should be separated by approximately the interval $a = {}^2\Pi_{\frac{1}{2}} - {}^2\Pi_{1\frac{1}{2}}$ of $(XY)^+$ (cf. section 3) from the two components $\Omega = 2$ and 1 derived from ${}^2\Pi_{1\frac{1}{2}}$. Transitions from the ${}^1\Sigma^+$ normal state of XY should occur to both the $\Omega = 1$ levels with about equal intensity, and to the $0^+$ level.

Since the $\sigma^x$ orbital should presumably have little bonding power, the molecular constants ($\omega_e$ and $r_e$) should not differ greatly for the excited levels of (13) from those of the normal state of $(XY)^+$. The latter in turn should not be radically different (cf. section 3), from the constants of the normal state of neutral XY, if expressions (5) and (7), using atomic (nonbonding) orbitals for the $\pi$ electrons are good approximations, as we believe.

Now Cordes and Sponer have found in the ultraviolet between λ1600 and λ2000, for each of the molecules ICl, IBr and BrCl, a pair of absorption band systems which agree in all respects with what we should expect for transitions to the states (16). In each case the two systems are almost alike in intensity, appearance, and in $\omega_e'$, and in the fact that $\omega_e'$ is 12–18 percent greater than $\omega_e''$ ($\omega_e''$ refers of course to the normal state of the molecule).

The upper levels of the two systems are tentatively classed by Cordes and Sponer as the ${}^3\Pi_1$ and ${}^3\Pi_0$ components of a ${}^3\Pi$. The observed intervals $\Delta\nu$ between the (0,0) bands of the two systems of each molecule (cf. Table IIA) are, however, larger than one could reasonably expect for a normal interval ${}^3\Pi_0 - {}^3\Pi_1$. For an ordinary triplet, one expects ${}^3\Pi_0 - {}^3\Pi_1 \approx {}^3\Pi_1 - {}^3\Pi_2 \approx \frac{1}{2}A$, where $A$ is the spin-orbit $(\Lambda - \Sigma)$ coupling coefficient.[7] To account for a ${}^3\Pi$ excited state of XY at the level observed, no reasonable electron configuration but one of the type $\sigma^2\pi^4\pi^3\sigma$ seems open. For such a ${}^3\Pi$, $A$ would be determined by the group $\pi^3$, and if the $\pi$ orbitals in $\pi^3$ are essentially atomic $np\pi$, as has been shown in section 3 to be entirely probable, then $A$ should be nearly the same as $a$ for $np$ of the corresponding atom ($a = 2({}^2P_{\frac{1}{2}} - {}^2P_{1\frac{1}{2}})/3$ for a halogen atom $np^5$, ${}^2P$). In short, for a state $\sigma^2\pi_Y{}^4\pi_X{}^3$, ${}^3\Pi$ of XY, $A$ should be about equal to $a$ of atom X, and ${}^3\Pi_0 - {}^3\Pi_1$ should be half this, or about one-third of (${}^2P_{\frac{1}{2}} - {}^2P_{1\frac{1}{2}}$). More precisely, something between $a$ of X and of $X^+$ might be expected. On this basis, we should predict ${}^3\Pi_0 - {}^3\Pi_1$ to be about 2700 in the cases of ICl and IBr, assuming that it is an I atom $\pi$ electron which is excited, and about 1300 for BrCl assuming a Br $\pi$ electron

TABLE IIA. *Multiplet intervals.*

| *Molecule*[a] | *Predicted*[b] | | *Observed* $\Delta\nu$(volts)[c] |
|---|---|---|---|
| | $\Lambda$–$\Sigma$ *coupling* | $\Omega$–$s$(*J–J-like*) *coupling* | |
| XY or $X_2$ | $\pi_Y{}^4\pi_X{}^3\sigma$ : ${}^1\Pi$; ${}^3\Pi_{0,\,1,\,2}$ | $[(\cdots\pi_Y{}^4\pi_X{}^3,\ {}^2\Pi_{\frac{1}{2}})]\sigma$ : ${}_{1,\,0}$<br>$[(\cdots\pi_Y{}^4\pi_X{}^3,\ {}^2\Pi_{1\frac{1}{2}})]\sigma$ : ${}_{1,\,2}$ | |
| | ${}^3\Pi_0-{}^3\Pi_1={}^3\Pi_1-{}^3\Pi_2$<br>$\approx\frac{1}{2}a_{X^+}$ or $\frac{1}{2}a_X$ | $({}^2\Pi_{\frac{1}{2}}\sigma)\Pi_{1,\,0}-({}^2\Pi_{1\frac{1}{2}}\sigma)\Pi_{1,\,2}\approx a_{X^+}$ or $a_X$ | |
| ICl (*uv*) | $\frac{1}{2}a_{I^+}=(0.344)$ : $\frac{1}{2}a_I=0.312$ | $a_{I^+}=(0.688)$; $a_I=0.625$ | $0.582=\Pi_{1,\,0^+}-\Pi_1$ |
| IBr (*uv*) | same as ICl | same as ICl | 0.576 " |
| BrCl (*uv*) | $\frac{1}{2}a_{Br^+}=(0.168)$; $\frac{1}{2}a_{Br}=0.152$ | $a_{Br^+}=(0.336)$; $a_{Br}=0.303$ | 0.276 " |
| ICl (*vis*) | as ICl above | as ICl above | $0.44=\Pi_{0^+}-\Pi_1$ |
| IBr (*vis*) | as ICl | as ICl | 0.50 " |
| $I_2$ (*vis*) | as ICl | as ICl | $0.68\pm0.05=\Pi_{0^+}-\Pi_1$ |
| $Br_2$ (*vis*) | as BrCl | as BrCl | 0.27 " |

*Notes for Table IIA.* (a) Here "*uv*" refers to the upper levels of the ultraviolet absorption bands near λ1800, "*vis*" to the well-known visible and infrared bands. (b) Values of $a$ for Br and I from $np^5$, ${}^2P$ : $a=2({}^2P_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}})/3$; for $Br^+$ and $I^+$ estimated (cf. section 3). (c) Data for visible bands are from Brown (Ref. 3, under IBr); for ultraviolet bands from Ref. 9. The values given refer to the interval between the *potential minima* of ${}^3\Pi_{0^+}$ and ${}^3\Pi_1$. This should give satisfactory results provided ${}^3\Pi_{0^+}$ and ${}^3\Pi_1$ have about equal $r_e$ and $\omega_e$ values, as is the case in the ultraviolet bands and very probably also in the visible, infrared bands (cf. Brown[3]). The $\Delta\nu$ values for the latter bands are, however, less certain than for the former, for experimental reasons (cf. Brown[3]) and also because of the fact that the ${}^3\Pi_{0^+}$ dissociates differently than the ${}^3\Pi_1$ and other components (${}^1\Pi$, ${}^3\Pi_{0^-}$, ${}^3\Pi_2$). This latter fact should tend to produce a relative distortion of the U(r) curve of ${}^3\Pi_{0^+}$. In the case of $I_2$ an independent, but probably less reliable value, of $\Delta\nu$ ($6060\ \text{cm}^{-1}=0.75$ volt) is obtained by taking the difference between the $\nu$ value of the intensity maximum of the ${}^3\Pi_{0^+}\leftarrow{}^1\Sigma^+_g$ continuum (λ5060) and that of the ${}^3\Pi_1\leftarrow{}^1\Sigma^+_g$ continuum (λ7320, Brown[2]).

excited (cf. Table II). The observed $\Delta\nu$ values, however, are 4713 for ICl, 4668 for IBr, and 2238 for BrCl, all much larger than expected for an ordinary ${}^3\Pi_0-{}^3\Pi_1$.

If, however, (cf. (16)), we interpret the lower-frequency system in each pair as having the upper electron level $\{[X^+Y,\ {}^2\Pi_{1\frac{1}{2}}]\sigma^x\}_1$, and the higher-frequency system as having $\{[X^+Y,\ {}^2\Pi_{\frac{1}{2}}]\sigma^x\}_{0^+,\,1}$, with the components $\Omega=0^+$ and 1 too close together to be resolved with the dispersion used, then the observed $\Delta\nu$'s agree rather well with what we should expect. The predicted $\Delta\nu$'s (somewhat less than $a$ of $X^+$) are now about 5400 for ICl and IBr, and about 2600 for BrCl. The observed values are 86 percent (BrCl) or 87 percent (ICl, IBr) as large as the predicted. The discrepancy of some 13 percent can be attributed to various influences which tend to modify the atomic or ionic $a$ when the atom or ion enters a molecule (cf. section 3).

Particularly striking is the close agreement between the $\Delta\nu$ values of ICl and IBr. This supports the idea that it is essentially an I atom $\pi$ electron which is excited in both cases, and that the use of atomic orbitals for the $\pi$ electrons in halogen molecules of the type XY, as in (5) and (7), is a good approximation. The $\Delta\nu$ of BrCl likewise agrees with the idea that it is the Br whose $\pi$ electron is excited.

At somewhat shorter wave-lengths than the bands here discussed are others,[9] apparently similar, which may be attributable to a more highly excited $\sigma^x$.

Accompanying the bands under discussion there is continuous absorption, increasing toward shorter wave-lengths. This has been attributed to dissociation and predissociation processes[9] resulting from the (expected) presence of repulsive potential energy curves of the molecule. Plenty of such curves are to be found among the states discussed in section 9; in particular, if Table IV should happen to be nearly correct, the $\sigma^2\pi^3\pi^3\sigma^{*2}$, ${}^3\Sigma^+$ and ${}^3\Delta_{1,\,2}$ states might cause predissociation of our $\sigma^2\pi^4\pi^3\sigma^x$, $\Pi$ states.

Certain strong $I_2$ absorption bands,[10] near λ1750, with $\omega_e'$ and $\omega_e''$ apparently about equal,

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[9] Vacuum and near λ2000 ultraviolet absorption of $Cl_2$, $Br_2$, ICl, IBr, BrCl: H. Cordes and H. Sponer, Zeits. f. Physik **63**, 334 (1930); **79**, 170 (1932).

[10] Vacuum ultraviolet $I_2$ bands: H. Sponer and W. W. Watson, Zeits. f. Physik **56**, 1841 (1929).

are presumably similar to the lower-frequency systems of ICl, IBr, and BrCl bands just discussed. If this interpretation is correct, the corresponding higher-frequency $I_2$ system should appear near λ1615. Sponer and Watson state[10] that strong absorption occurs in the region from λ1600–λ1500, but was observed only qualitatively because of the failure of the continuous source there. Later, Cordes and Sponer at the end of their 1932 paper[9] indicate briefly that the relations in $I_2$ have been further studied, and are indeed similar to those in ICl and the rest. The analogous bands of $Br_2$ and $Cl_2$ probably lie below λ1600.

It is of interest to inquire why the $\omega_e'$ values are larger than the $\omega_e''$ in the XY bands ($\omega_e'/\omega_e''=1.12$ in the ICl bands, 1.15 in IBr, 1.18 in BrCl). A reasonable explanation would be that the $\sigma^x$ orbital has an appreciable bonding power. Other factors, however, such as bonding action of the group $\pi^4\pi^3$ of $X^+Y$, or changes in heteropolar forces, may also contribute.

Another point of interest is the term value (ionization energy) of $\sigma^x$. If the predicted ionization potentials of ICl, IBr, BrCl in Table I should be correct (11.16, 11.16, and 12.43 volts, respectively, for removal of $\pi_X$ to give *mean* of ${}^2\Pi_{1\frac{1}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$), then the $\sigma^x$ term values (cf. Table I) are, respectively, 4.26, 4.49, and 4.97 volts. These are of the right order of magnitude, but decidedly higher than we expect if $\sigma^x$ is essentially an atomic orbital. This may be due partly to bonding properties of $\sigma^x$ suggested above, or it may also be that the predicted $I$ values of ICl, IBr, BrCl used above are somewhat (perhaps about 1 volt) larger than the actual values.

In the $I_2$ bands near λ1750, $\omega_e'$ and $\omega_e''$ appear to be about equal. This difference as compared with the XY bands may be due to the necessity of having the $I_2^+$ core in the (somewhat excited) form ${}^2\Pi_u$ in order to satisfy the $g \longleftrightarrow u$ selection rule (cf. (17)). The ${}^2\Pi_u$ core should have a somewhat larger $r_e$ and smaller $\omega_e$ than neutral $I_2$ if the ${}^2\Pi_u - {}^2\Pi_g$ interval is appreciable (cf. section 4). This tendency, counterbalanced by a mild bonding effect of the $\sigma^x{}_g$ orbital, might well produce a resultant state with $r_e$ and $\omega_e$ about the same as for the normal state of $I_2$.

## 7. Ω–*s* coupling in halogen molecules: infrared, visible bands

The preceding explanation of the $\Delta\nu$'s in the vacuum ultraviolet XY bands receives strong support from the $\Delta\nu$ data on the Π upper levels of the infrared and visible band-systems of XY and $X_2$. These upper levels have been interpreted[1, 2] as a ${}^3\Pi_1$ (infrared bands, mostly) and a ${}^3\Pi_{0^+}$ (visible bands) belonging to an upper electron configuration $\sigma^2\pi^4\pi^3\sigma^*$ (cf. (11)), except that the formulation $\pi_Y{}^4\pi_X{}^3\sigma^*$ for molecules XY has not heretofore been clearly stated. The electron configuration here is exactly like that attributed to the upper levels of the vacuum ultraviolet bands (cf. (16), (17)) except that we have $\sigma^*$ instead of $\sigma^x$.

As will be seen from the $\Delta\nu$ data in Table IIA, the interval $\Pi_{0^+} - \Pi_1$ in $I_2$ and $Br_2$ corresponds well to Ω–*s* coupling as in the ultraviolet bands. In IBr and especially ICl, the $\Delta\nu$ values are smaller than in the ultraviolet bands, suggesting that the coupling departs appreciably from the Ω–*s* type. It seems likely that Ω–*s* coupling is incomplete also in $Br_2$ and $I_2$, and that their relatively large $\Delta\nu$'s are partly a result of a strong tendency toward case *c*.[1]

It will be of great interest to look for the ${}^3\Pi_1 \leftarrow {}^1\Sigma^+$ bands of $Cl_2$, in order to determine the $\Delta\nu({}^3\Pi_{0^+} - {}^3\Pi_1)$ and thus see whether Ω–*s* coupling still persists. Data on BrCl, ClF, and $F_2$ would of course also be of interest.

The preceding results lead to the prediction that a ${}^3\Pi_2$ should in each case be close below the ${}^3\Pi_1$, and a ${}^1\Pi$ close above the ${}^3\Pi_0$, especially in $I_2$. The question of the existence of transitions to the ${}^1\Pi$ will be discussed in the next section.

Ω–*s* coupling, of course, means that the Π upper levels, although for convenience we shall continue to designate them as ${}^3\Pi_1$, ${}^3\Pi_{0^+}$, ${}^1\Pi$, etc., are really not definitely either singlet or triplet. Further, the case *c* tendency makes even the classification as Π levels not quite sharp.

With nearly Ω–*s* coupling, we expect ${}^3\Pi_1 \leftarrow {}^1\Sigma^+$ and the predicted ${}^1\Pi \leftarrow {}^1\Sigma^+$ should have about equal intensity, ${}^3\Pi_1 \leftarrow {}^1\Sigma^+$ getting relatively weaker, however, in the lighter halogens if these should tend strongly away from Ω–*s* toward Λ–Σ coupling. The observed, on the whole very weak, ${}^3\Pi_1 \leftarrow {}^1\Sigma^+$ transitions in the heavier halogens may then probably be assumed equal to the $^1\Pi \leftarrow {}^1\Sigma^+$ in intensity, and so may probably be taken approximately as a true measure of the natural intensity of the transition from the normal electron configuration $\sigma^2\pi^4\pi^4$ to the excited configuration $\sigma^2\pi^4\pi^3\sigma^*$.

The much greater strength of the $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ transitions must be accounted for in some other way, as will be shown in a moment. Van Vleck has suggested that these transitions probably get their intensity mainly because $^3\Pi_{0^+}$($^3\Pi_{0^+u}$ in $X_2$) steals from a higher-energy $^1\Sigma^+$($^1\Sigma^+_u$ in $X_2$) which combines very strongly with the $^1\Sigma^+$ ($^1\Sigma^+_g$ in $X_2$) normal state. Such stealing, corresponding to mutual perturbation and partial mixing of wave functions of $^3\Pi_{0^+u}$ and $^1\Sigma^+_u$ (in $X_2$), could readily occur in view of the $\Omega$–$s$ type of coupling in the $^3\Pi_{0^+}$, both states being of type $0^+_u$. In the case of $I_2$, Van Vleck tentatively identifies the $^1\Sigma^+_u$ state in question as the "*D*" state, and the $^1\Sigma^+_u \leftarrow {}^1\Sigma^+_g$ as the well-known and extensive band-system near λ2000. As we shall see in section 9, this is very reasonable. The reader may wonder why we *must* attribute the $^3\Pi_{0^+u} \leftarrow {}^1\Sigma^+_g$ intensity mainly to perturbation by another state. This is simply because, with $\Omega$–$s$ coupling in the $\Pi$ states, we could not otherwise account for the great difference in intensity between $^3\Pi_1 \leftarrow {}^1\Sigma^+$ and $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$. If both were unperturbed, the former should be about twice as intense as the latter. Since perturbations are not likely to decrease, but only to increase, a low intensity, we conclude that the intensity of $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ must probably have been increased by a perturbing influence.

As Van Vleck has pointed out, the abnormally high intensity of the $^3\Pi_{0^+u} \leftarrow {}^1\Sigma^+_g$ might be due to a strong perturbation either of the $^3\Pi_{0^+u}$ or of the $^1\Sigma^+_g$, or of both; he concluded, however, that it is essentially only perturbation of the $^3\Pi_{0^+u}$ which is responsible for the high intensity. We are now in a position to reconsider the matter, in view of our increased understanding of the halogen molecules (cf. results and predictions summarized in Table III, and discussed in section 10).

It seems probable that the normal state $\sigma^2\pi^4\pi^4$, $^1\Sigma^+_g$ of $I_2$ is strongly perturbed by the predicted $\sigma^2\pi^3\pi^4\sigma^*$, $^3\Pi_{0^+g}$, which should have $\Omega$–$s$ coupling and probably is located about 3 volts above the normal state (cf. Table III and section 10). Now the $\sigma^2\pi_u{}^3\pi_g{}^4\sigma^*$, $^3\Pi_{0^+g}$ may well combine strongly with the $\sigma^2\pi_u{}^4\pi_g{}^3\sigma^*$, $^3\Pi_{0^+u}$ (cf. the very strong combination of $\sigma^2\pi_u{}^4\pi_g{}^2$, $^3\Sigma^-_g$ with $\sigma^2\pi_u{}^3\pi_g{}^3$, $^3\Sigma^-_u$ in $O_2$,—the Schumann-Runge bands), hence strong perturbation of $^1\Sigma^+_g$ by $^3\Pi_{0^+g}$ should enable the former to combine readily with $^3\Pi_{0^+u}$; but need not much strengthen $^3\Pi_{1u} \leftarrow {}^1\Sigma^+_g$, since $^3\Pi_{0^+g}$ may combine only weakly with $^3\Pi_{1u}$ (cf. discussion of selection rules following (17)). It seems likely that this perturbation of $'\Sigma^+_g$ by $^3\Pi_{0^+g}$ may be the main reason for the strong combination of $^1\Sigma^+_g$ with $^3\Pi_{0^+u}$, rather than perturbation of the $^3\Pi_{0^+u}$ by $^1\Sigma^+_u$. In general, of course, the intensity of perturbation of a state $A$ by a state $B$ depends on $H_{AB}/(H_B - H_A)$. Now $H_B - H_A$ is decidedly smaller for the $^1\Sigma^+_g$ and $^3\Pi_{0^+g}$ than for $^3\Pi_{0^+u}$ and $^1\Sigma^+_u$, and it seems probable also that $H_{AB}$ is larger; arguments for this will be given below. The foregoing discussion applies, of course, to homopolar molecules $X_2$, but somewhat similar considerations apply to XY molecules.

However this may be, a difficulty is the surprisingly low intensity of the $^3\Pi_1 \leftarrow {}^1\Sigma^+$ transitions, which suggests that these would be forbidden but for some weak perturbing influence, whereas the assumed electron configurations, which appear almost inevitable in our theory, would incline us (for $\Omega$–$s$ coupling) to expect a strong transition. This weakness may be attributable simply to smallness of overlapping of the $\pi$ and $\sigma^*$ orbitals of initial and final state wave functions, but the matter appears to deserve further study (cf. also Van Vleck[4]).

The increasing intensity of $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ in the order $Cl_2$, $Br_2$, $I_2$ (cf. Table IIB) has formerly been attributed to the usual increase in probability of an intersystem combination with increasing atomic weight (tendency toward *J*–*J*-like, i.e., $\Omega$–$s$, coupling). Under ordinary circumstances (coupling still nearly *L*–*S*-like) the intensity of singlet-triplet, as compared with singlet-singlet, combinations is about proportional to $(\delta\nu/\Delta\nu)^2$, where $\delta\nu$ is the width of the triplet (proportional to $a$) and $\Delta\nu$ is the interval between the triplet and corresponding singlet (cf. $^3\Pi$ and $^1\Pi$ in our case). Qualitatively, the observed intensities agree with this. Since, however, the coupling has been shown to be nearly

TABLE IIB. *Intensity data on* $\sigma^2\pi^4\pi^3\sigma^*$, ${}^3\Pi \leftarrow \sigma^2\pi^4\pi^4$, ${}^1\Sigma^+$ *bands.*

| $\Omega$ of ${}^3\Pi$ | | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ | ICl | IBr |
|---|---|---|---|---|---|---|---|
| $0^+$ | $\lambda_{conv.}$ | — | 4785 | 5106 | 4991 | (5481) | (5450) |
| | $\lambda_{max.}$ | 2900 | 3300 | 4100 | 5060, 5575 | 4700 | 4950 |
| | $\nu_{\frac{1}{2}max.}$ | 41,500 | 33,100 | 26,400 | 20,800 | 24,100 | — |
| | $\nu_{max.}$ | 34,500 | 30,300 | 24,400 | 19,800 | 21,300 | — |
| | $\nu_{\frac{1}{2}max.}$ | 29,500 | 27,800 | 20,000 | 17,200 | 19,600 | — |
| | $k_{max.}$ | 0.542 | 6.8 | 16.6 | 93.7 | 8.7 | — |
| | $[P/e]$ in A | 0.026 | 0.067 | 0.13 | 0.26 | 0.083 | — |
| 1 | $\lambda_{conv.}$ | — | — | 6291 | 8039 | 5758 | 6820 |
| | $\lambda_{max.}$ | — | — | — | 7320 | [near $\lambda_{conv.}$] | [near $\lambda_{conv.}$] |
| | $k_{max.}$ | — | — | (much?) less than $0^+$; stronger ($\times 5$?) than for 1 of $I_2$ | very much less than for $0^+$ | $<10\%$ as strong as $0^+$ | Ratio to $0^+$ nearly like ICl |

*Notes for Table IIB.* $\lambda_{conv.} = \lambda$ of convergence limit of vibrational levels (data from references 2, 3); this is given for comparison with $\lambda_{max.} = \lambda$ of maximum absorption, which is usually, but not always, in the continuum above the convergence limit. $0^+ = {}^3\Pi_{0^+}$, $1 = {}^3\Pi_1$. $\lambda_{\frac{1}{2}max.} =$ two $\lambda$ values at which $k$ has fallen to one-half of $k_{max.}$; $k =$ absorption coefficient defined by $I = I_0 e^{-kl}$, where $l =$ path in cm; $I$, $I_0 =$ light intensity; $k$ values here recalculated to basis of ideal vapor at 0°C and 760 mm pressure. Data on $\lambda_{max.}$, $\lambda_{\frac{1}{2}max.}$, and $k_{max.}$ are based on: $F_2$, v. Wartenberg et al.[12]; $Cl_2$, v. Halban and Siedentopf and Gibson, Bayliss and Rice[11]; $Br_2$ ${}^3\Pi_{0^+}$, Ribaud[11]; $Br_2$ ${}^3\Pi_1$, private communication from W. G. Brown (also cf. reference 2); $I_2$ ${}^3\Pi_{0^+}$, K. Vogt and J. Königsberger, Zeits. f. Physik **13**, 294 (1923)[11]; $I_2$ ${}^3\Pi_1$, W. G. Brown[2]; ICl ${}^3\Pi_{0^+}$, G. E. Gibson and H. C. Ramsperger, Phys. Rev. **30**, 603 (1927); ICl ${}^3\Pi_1$, interpretation of Brown and Gibson[3], according to which $\lambda_{max.}$ is near $\lambda_{conv.}$ for ${}^3\Pi_1$ and, if so, $k_{max.}$ of ${}^3\Pi_1$ is so small as to be obscured by the curve of $k$ against $\lambda$ sloping upward to $k_{max.}$ of ${}^3\Pi_{0^+}$ (cf. Fig. 2 of Gibson and Ramsperger); IBr, cf. reference 3, especially Brown. $P =$ effective electric moment of electronic transition, $P/e =$ corresponding effective amplitude of a vibrating electron. The $P/e$ values have been calculated from $P/e = 0.0619 \times 10^{-8} (\int k_\nu d\nu/\nu)^{\frac{1}{2}}$, using as an approximation for $\int k_\nu d\nu/\nu$ the expression $k_{max.}\Delta\nu/\nu_{mean}$, where $\Delta\nu$ is the interval between the two positions $\nu_{\frac{1}{2}max.}$, and $\nu_{mean}$ is their mean; the approximation is a good one if, as here, the $k-\nu$ graph is approximately triangular in shape.

The $k$ given above for $I_2$ is based on low-pressure data of Vogt and Königsberger ($t$ = 48°C, vapor density $2.54 \times 10^{-5}$ g/cc), since these authors find that Beer's law fails for vapor densities above $4 \times 10^{-5}$ in $I_2$; data for higher densities give much lower $k$ values. Conceivably, however, there is some hidden source of error in the low-pressure data, since the failure of Beer's law occurs at the same pressure and to the same extent in the region of discrete bands as in the continuum. Work of Plumley, however (Phys. Rev. **45**, 678 (1934)) tends to support the high ratio of $k$ for $I_2$ as compared with $Br_2$ (the high-pressure data of V. and K. would give a much lower ratio). The data used for $k$ of $Br_2$ ($p = 66$ mm Hg) are in the region of validity of Beer's law, according to Ribaud and V. and K. Presumably this is true also of $Cl_2$ and $F_2$.

The low-pressure data of V. and K. on $I_2$ show a secondary maximum of $k$ in $I_2$ at about $\lambda 5575$. At higher pressures, this shifts somewhat and finally disappears, leaving only a wave and a shoulder in the $k$–$\lambda$ curve.

In regard to the ${}^3\Pi_1 \leftarrow {}^1\Sigma^+$ infrared bands of $Br_2$ and $I_2$, Dr. W. G. Brown states (private communication) that these are stronger at 200 mm pressure in $Br_2$ than at 760 mm pressure in (hot) $I_2$, for the same path-length. Also he states that the continuum of these bands in $Br_2$, at high pressures, blots out the visible bands, while an analogous phenomenon does not occur in $I_2$. (This, of course, can be partly accounted for because the visible bands are weaker in $Br_2$ than in $I_2$.)

$\Omega$–$s$, modified by a case $c$ tendency, the foregoing relations do not apply, and the observed increase in intensity with atomic weight must probably be attributed to other causes (variation in perturbation index $H_{AB}/(H_B - H_A)$, itself probably due, however, largely to the increase in case $c$ tendency, hence in $H_{AB}$, with atomic weight (cf. fourth following paragraph)).

It is instructive to express the intensities of the various ${}^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ transitions in terms of amplitude of vibration $P/e$ of corresponding electric moment $P$($e$ = electronic charge). For $Cl_2$, Gibson, Bayliss and Rice[11] obtain for $P/e$ the value $0.016 \times 10^{-8}$ cm, but there appears to have been an error in the calculation. For, using the simple relation $P/e = 0.0619 \times 10^{-8} (\int k_\nu d\nu/\nu)^{\frac{1}{2}}$, one gets $P/e = 0.067 \times 10^{-8}$ cm $= 0.067$A for $Cl_2$, in disagreement with their result. Values for the other halogens calculated using the above formula range from 0.026A for $F_2$ to 0.26A for $I_2$ (cf. Table IIB). As a comparison, the value 0.50A

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[11] For absorption intensity data on $I_2$, $Br_2$, $Cl_2$, cf. International Critical Tables, Vol. V, p. 269; $Cl_2$, also G. E. Gibson, N. S. Bayliss and O. K. Rice, Phys. Rev. **44**, 188, 193 (1933).

TABLE III. *Predicted electronic states of $I_2$.*

| *Est. mean vertical energy*[a] | *Elec. Config.* in terms of molecular orbitals; numbers of | | | | *Electron States*[b] | | | *Dissociation*[c] | | *Elec. Config.* in terms of atomic orbitals | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\sigma_g$ | $\pi_u$ | $\pi_g$ | $\sigma_u$ | Parity | Case *a* or *b* or Ω–*s* type | Case *c* type | Products | Energy (volts) | Atom A | Atom B |
| 12 | 0 | 4 | 4 | 2 | *g* | $^1\Sigma^+$ | $0^+$ | *ex* | | $5p\sigma^2\ 5p\pi^4$ | $5p\pi^4$ |
| 8.8 | 1 | 3 | 4 | 2 | *u* | $^{1,\,3}\Pi$ | $1,0^-,0^+,1,2$ | *ex* | | $\sigma^2\pi^4$ | $\sigma\pi^3$ |
| 8.1 | 1 | 4 | 3 | 2 | *g* | $^{1,\,3}\Pi$ | ,, | *ex* | | | |
| 7.3 | 2 | 3 | 4 | $\sigma^{\times}_g$ and others | *u* | $\Pi$ | ,, | *ex* | | $\sigma\pi^4$ | $\sigma\pi^3\ 6s$ |
| 6.1 | 1 | 4 | 4 | 1 | *u* | $^1\Sigma^+$ | $0^+$ | *ex* | | $\sigma^2\pi^4$ | $\pi^4$ |
| | | | | | | $^3\Sigma^+$ | 1<br>$0^-$ | *bb**<br>*bb* | | $\sigma\pi^4$ | $\sigma\pi^4$ |
| 5.6 | 2 | 2 | 4 | 2 | *g* | $^1\Sigma^+$, $^1\Delta$, $^3\Sigma^-$ | $0^+$, $2,0^+,1$ | *ex* | | $\sigma^2\pi^4$ | $\sigma^2\pi^2$ |
| 4.9 | 2 | 3 | 3 | 2 | *u* | $^1\Sigma^+$<br>$^1\Delta$<br>$^3\Sigma^-$ | $0^+$<br>2<br>$0^+$<br>1 | *ex*<br>*ex*<br>*ex*<br>*ex** | 8.28 | | |
| | | | | | | $^3\Sigma^+$<br>$^3\Delta$<br>$^1\Sigma^-$ | $0^-,1$<br>1,2<br>3<br>$0^-$ | *ab*<br>*ab*<br>*aa*†<br>*aa* | | $\sigma^2\pi^3$ | $\sigma^2\pi^3$ |
| 4.2 | 2 | 4 | 2 | 2 | *g* | $^1\Sigma^+$<br>$^1\Delta$, $^3\Sigma^-$ | $0^+$<br>$2,1,0^+$ | *bb*<br>*ab* | 3.42 | | |
| 2.8 | 2 | 3 | 4 | 1 | *g* | $^1\Pi$<br>$^3\Pi$ | 1<br>$0^-$<br>$0^+,1,2$ | *ab*<br>*ab*†<br>*aa* | | $\sigma^2\pi^3$ | $\sigma\pi^4$ |
| 2.1 | 2 | 4 | 3 | 1 | *u* | $^1\Pi$<br>$^3\Pi$ | 1<br>$0^+$<br>$0^-,1,2$ | *aa*<br>*ab*†<br>*aa* | 2.48 | | |
| 0.0 | 2 | 4 | 4 | 0 | *g* | $^1\Sigma^+$ | $0^+$ | *aa* | 1.54 | $\sigma\pi^4$ | $\sigma\pi^4$ |

*General notes for Table III.* The electron configuration of each electron state is expressed at the left of the table wholly in terms of *molecular orbitals* for the ten outer electrons (cf. (4a) in section 1; and note that by $\sigma_u$ is meant $\sigma^*_u$ of section 5 (cf. (12)), except in one case where $\sigma^{\times}_u$ of (15) is meant). Of course it is to be understood that such "pure electron configurations" have only an approximate meaning (cf. section 1) and that the actual states involve mixtures of these but usually with one configuration predominant. At the right of Table III the best pure electron configurations in terms wholly of *atomic orbitals* are given for the same electron states; it will be noticed that part of these belong to I+I, part to $I^+ + I^-$. *Mixed* electron configuration descriptions using molecular orbitals for shared ($\sigma$) and atomic orbitals for nearly unshared ($\pi$) electrons, such as have been used for the most part in this paper, and constitute probably the best pure electron configuration approximations, can be readily written by taking the $\sigma$ parts of the electron configuration of any state from the left of the table, the $\pi$ parts from the right. The electron states listed in Table III include *all* states derivable by combining two iodine atomic electron configurations containing ten $5p$ electrons between them, *viz.*, $I(p^5)+I(p^5)$ and $I^-(p^6)+I^+(p^4)$. Exactly analogous tabulations would of course hold for $Br_2$, $Cl_2$ and $F_2$. It should be noted that the case *a* or *b* or Ω–*s* type classification of electron states has a well-defined meaning only for fairly small *r* values, while the case *c* classification is applicable for large *r* values, and is important for dissociation product correlations.

The forms of the $U(r)$ curves of the various states listed in Table III can be roughly predicted from the vertical excitation energy given in the first column, combined with the predicted dissociation energies given in the "dissociation" column, together with a consideration of the nature of the $\sigma$ orbitals present. The bonding type $\sigma_g$ tends to make the minimum, if any, of the $U(r)$ curve come at relatively small $r$ values, the anti-bonding type $\sigma^*_u$ to make it come at large $r$ values. The $\pi$ types should also have some effect, $\pi_u$ and $\pi_g$ being, respectively, a little bonding and anti-bonding.

*Special notes for Table III.*[a] These estimates are based on assumed mean excitation potentials of 2.1 volts for $\pi_u \rightarrow \sigma_u$, 6.1 volts for $\sigma_g \rightarrow \sigma_u$, and 0.7 volt for $\pi_g \rightarrow \pi_u$. The value 2.1 is based on data on the visible bands, 6.1 on the rough value

6.5 volts for $\sigma_g\pi_u^4\pi_g^4\sigma_u$, ${}^1\Sigma^+_u \leftarrow \sigma^2\pi^4\pi^4$, ${}^1\Sigma^+_g$, assuming that the *D* level of $I_2$ may be identified as this ${}^1\Sigma^+_u$ (cf. *E* values in Table I); the value 0.7 is a guess. The value 7.3 for $\pi_u \rightarrow \sigma^\times_g$ is based on the observed value $\sim$ 7.05 volts for the process (λ1750) here tentatively identified as $\sigma^2\pi^3\pi^4\sigma^\times_g$, ${}^3\Pi_{1u} \leftarrow \sigma^2\pi^4\pi^4$, ${}^1\Sigma^+_g$. It should be especially noted that the estimates given refer to *vertical* excitation energies; in the case of all states which are not repulsive, the minimum excitation energy, to minimum of *U*(*r*) curve, must be less.—One should of course not place too much reliance on these energy estimates. [b]The electron states associated with each electron configuration are given in their probable order of energy, as indicated by theoretical considerations and by experimental data on molecules with similar configurations. Innumerable other excited states of $I_2$ must exist, derivable from $I+I$, $I^+ + I^-$, $I^{++} + I^{=}$ etc. with one or more atomic electrons excited out of their normal orbits. [c] Under "dissociation products," *aa* means *a*+*a*, and so on, where *a* means $I(5p^5, {}^2P_{1\frac{1}{2}})$ and *b* means $I(5p^5, {}^2P_{\frac{1}{2}})$; *ex* means one atom, at least, with an excited electron, or else $I^+(p^4)+I^-(p^6)$. The three cases marked with a dagger are "unique states" (cf. reference 1, p. 1445) which practically *must* dissociate in the manner indicated. In the other cases marked *aa*, *ab*, or *bb*, there is always a possibility (except in cases where the correlation is experimentally known) that the state may tend strongly to dissociate into products with more energy than those predicted by the strict case *c* rules, which assume that no crossing of *U*(*r*) curves of states of identical case *c* type can take place (cf. reference 1, pp. 1449–50 and reference 4, p. 567 in regard to reasons why such tendencies may exist; and Brown and Gibson[3] and Brown[3] for an example of such a case in ICl and IBr). The predicted dissociation correlations given in the table may, of course, also be subject to partial alteration if, as is highly probable, the energy order of some of the levels is different from that estimated. The dissociation correlations marked* in the table require the crossing of two *U*(*r*) curves of the same case *c* type ($1_u$), contrary to the strict rules; this *may* be incorrect, but the two states thus marked are so unlike in electron configurations that the occurrence of an effective crossing seems probable.

obtained by Stueckelberg[12] for the very intense Schumann ultraviolet $O_2$ band-system (mostly continuum) may be noted. This value 0.50 is also obtained very simply by using the above formula, thus checking Stueckelberg's result.

The above expression for *P*/*e* is obtained as follows. One readily finds that the absorption probability coefficient *B* for a frequency $\nu$ is given by $Bd\nu = (c/hn)(k_\nu d\nu/\nu)$, where $n$ = molecules/cc, $k$ = absorption coefficient. For the total probability connected with a given electron transition, we may take $\int Bd\nu = (c/hn)(\int k_\nu d\nu/\nu)$. The associated electric moment *P* is given by $P^2 = (3h^2/8\pi^3)\int Bd\nu$. From these relations, putting in numerical values, if *k* corresponds to gas at 0°C, 760 mm, one gets the above expression for *P*/*e*.

The notably large *P*/*e* value for $I_2$ means a really strong transition and so implies a very strong perturbation of ${}^3\Pi_{0^+u}$ by its presumed interaction with the ${}^1\Sigma^+_u$ above it, or of ${}^1\Sigma^+_g$ by the ${}^3\Pi_{0^+g}$ above it. In the former case, the ${}^3\Pi_{0^+u}$ should be pushed down, enough to make the interval up from ${}^3\Pi_{1u}$ to ${}^3\Pi_{0^+u}$ abnormally small; in the latter case the ${}^1\Sigma^+_g$ should be pushed down, but the position of the ${}^3\Pi_{0^+u}$ left unaffected. Actually the ${}^3\Pi_{0^+u} - {}^3\Pi_{1u}$ interval is a trifle larger, if anything, than we should expect even for ideal $\Omega$–*s* coupling. This may then be taken as evidence that, as was suggested above, it is mainly the ${}^1\Sigma^+_g$, rather than the ${}^3\Pi_{0^+u}$, which is perturbed.

The strong mutual perturbation of ${}^1\Sigma^+_g$ and ${}^3\Pi_{0^+g}$ inferred above can be understood in terms of the recognized strong tendency toward case *c* coupling[1] in the halogens, especially $I_2$. In case *c*, $\Lambda$ is no longer a good quantum number, and the pure ${}^1\Sigma^+_g$ and ${}^3\Pi_{0^+g}$ wave functions tend to become more or less mixed, both being of the case *c* type $0^+_g$. Such mixing is especially to be expected since the two $0^+_g$ states in question are the only ones derived from the union of two ${}^2P_{1\frac{1}{2}}$ X atoms (cf. Table III).

A peculiarity of the absorption curve of *k* against λ for $I_2$, as measured by Vogt and Königsberger, is the appearance, but only at very low vapor densities, of a secondary maximum of intensity at longer wave-lengths than the chief maximum, in the midst of the discrete bands (cf. Table IIB, and its notes). Further investigation may be desirable, especially since an unexplained failure of Beer's law beginning at low vapor densities has been found (Table IIB, notes). It may also be worth noting that the $k-\lambda$ curve of $Br_2$, like that of $I_2$, but unlike those of the lighter halogens, is broader on the long-λ than on the short-λ side of $k_{max.}$ (cf. data on $\nu_{\frac{1}{2}max.}$ in Table IIB). A possible explanation would be that the perturbing effect of ${}^3\Pi_{0^+g}$ on ${}^1\Sigma^+_g$ is greater for larger *r* values, where their *U*(*r*) curves approach each other; this would tend to increase the intensity of the longer-λ

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[12] E. C. G. Stueckelberg, Phys. Rev. **44**, 234 (1933).

regions of absorption, especially if absorption from excited states ($v''=1$, 2) is important, as in $I_2$.

From the data on the infrared, visible bands and their correlated continua, excitation energy data are available (cf. Table I), from which we can get approximate term values for the $\sigma^*$ orbital in the various molecules. The $\sigma^*$ vertical term value proves to be about 9 volts in all cases (cf. Table I), but is somewhat uncertain because of the uncertainty in the $I$ values of XY noted at the end of section 6. More definite are the excitation energies $E$ for $\sigma^2\pi^4\pi^4\rightarrow\sigma^2\pi^4\pi^3\sigma^*$, which show indications of interesting regularities. According to the discussion in earlier sections, the $\pi$ orbital which is here excited is probably approximately an I atom $\pi$ orbital in $I_2$, ICl, IBr, a Br atom $\pi$ orbital in $Br_2$ and BrCl, and so on, while the $\sigma^*$ excited orbital is predominantly (cf. section 5) $\sigma_I$ in $I_2$, IBr, and ICl, $\sigma_{Br}$ in $Br_2$ and BrCl. In harmony with these ideas, the $E$ values for $I_2$, IBr, ICl are nearly alike, as are those of $Br_2$ and BrCl; but in each series, the $E$ values increase as the second atom in the molecule gets lighter, as we might expect.

## 8. Absorption ${}^1\Pi\leftarrow{}^1\Sigma^+$ related to the visible and infrared bands?

As we have seen in section 7, the existence of nearly $\Omega$–$s$ coupling in the heavier halogen molecules requires that the transition ${}^1\Pi\leftarrow{}^1\Sigma^+$ should occur with approximately the same intensity as, or slightly greater intensity than, the ${}^3\Pi_1\leftarrow{}^1\Sigma^+$, and also indicates that the ${}^1\Pi$ level should lie, at small $r$ values, close above ${}^3\Pi_{0^+}$. According to the usual rules,[12a] the ${}^1\Pi$ $U(r)$ curve should give ${}^2P_{1\frac{1}{2}}+{}^2P_{1\frac{1}{2}}$ on dissociation, and would then be repulsive in character, or at most would have a very shallow minimum, for all the molecules XY and $X_2$ heavier than $Cl_2$ (cf. $U(r)$ curves of known states of these molecules[2, 3]). The absorption ${}^1\Pi\leftarrow{}^1\Sigma^+$ would then be continuous, and would be superposed on the continuum associated with ${}^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$. Being much weaker than the latter, it would not appreciably affect the appearance of the observed absorption curves. This is in agreement with observation: nothing about the observed continua of $F_2$, $Cl_2$, $Br_2$, or ICl (cf. Table IIB) gives any indication of compositeness; the secondary maximum in the $I_2$ absorption curve at long wave-lengths, noted in section 7, can hardly be attributed to ${}^1\Pi\leftarrow{}^1\Sigma^+$, because it occurs at too long $\lambda$ (and is too intense, if the present ideas are correct).

In the case of $Cl_2$, Gibson, Bayliss, and Rice have measured the absorption curve with great care, and found that its form could be calculated quantum-mechanically using for the upper level a $U(r)$ curve which can be joined on rather well to the known lower part of the ${}^3\Pi_{0^+u}$ curve of $Cl_2$, as determined from the discrete bands. Nevertheless, the observed curve is a little higher than the ${}^3\Pi_{0^+u}$ Morse curve, and might, so far as its form is concerned, equally well belong to the expected ${}^1\Pi_u$, which would then probably have a shallow minimum, and should then give rise to a few weak discrete absorption bands. If $Cl_2$ has nearly $\Omega$–$s$ coupling, the fact that ${}^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$, but not yet ${}^3\Pi_1\leftarrow{}^1\Sigma^+$, bands have been found, would indicate that ${}^1\Pi\leftarrow{}^1\Sigma^+$ must be relatively weak and that the observed continuum is mainly ${}^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$. Systematic comparison of the absorption curves for the $Cl_2$, $Br_2$, and $I_2$ continua supports this. In this connection, it may, however, be noted that ${}^3\Pi_1\leftarrow{}^1\Sigma^+$, according to Brown (Table IIB), is considerably stronger in $Br_2$ than in $I_2$.

On the whole, it seems probable that the

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[12a] The first report on the $F_2$ absorption spectrum appears to be that given by H. G. Gale and G. S. Monk (Phys. Rev. **29**, 211A, 1927), who state briefly that absorption occurs from about $\lambda$4100, using tubes from 7 mm to 3 cm long at 1 atm. Their (unpublished) photographs show the maximum of absorption to be near $\lambda$2900. Later T. R. Hogness (unpublished private communication) investigated the $F_2$ absorption up to several atmospheres pressure and 200° or 300°C in a 3 m tube and found evidence of discrete bands (apparently diffuse) near $\lambda$4500, H. von Wartenberg, G. Sprenger and I. Taylor [Göttinger Nachr. 1930, p. 119, and Bodenstein-Festband, p. 61 (Ergänzungsband of the Zeits. f. physik. Chemie, Leipzig, 1931)], measured the absorption coefficient of $F_2$ in the ultraviolet, finding the maximum absorption at $\lambda$2900, with $k$ as noted above in Table IIB. [Their citation of previous work on $I_2$ seems inaccurate; they use the higher-pressure $k$ for $I_2$ (cf. reference 11).] The absorption spectrum of $F_2$ has also been studied by G. E. Gibson and W. G. Brown and by R. Grinfeld and F. A. Jenkins (unpublished, private communications.)

Gale and Monk have also reported a continuous or nearly continuous emission spectrum in the ultraviolet, with two maxima, near $\lambda$2600 and $\lambda$2800. Examination of their plates (unpublished details) suggests a resemblance to the ultraviolet $I_2$ semi-continuous emission bands. Gale and Monk (l.c. and Astrophys. J. **69**, 77 (1929)) have also re-reported and analyzed a ${}^1\Sigma\rightarrow{}^1\Pi$ (either ${}^1\Sigma^+{}_u\rightarrow{}^1\Pi_g$ or ${}^1\Sigma^-{}_g\rightarrow{}^1\Pi_u$) system of $F_2$ emission bands. W. G. Brown (private communication) considers that these bands really comprise two or three systems. No obvious interpretation of the ${}^1\Sigma$ and ${}^1\Pi$ levels in terms of electron configurations (cf. Table III for $I_2$) is at hand.

observed ultraviolet continuum is still mainly ${}^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$ even in $F_2$, although it seems somewhat remarkable that in so light a molecule as $F_2$, such an intersystem transition should exceed the corresponding ${}^1\Pi\leftarrow{}^1\Sigma^+$ in intensity. A considerable persistence of tendency toward case *c* coupling is needed to account for this. Further investigation of the $Cl_2$ and $F_2$ absorption spectra will be of great interest in this connection.

In connection with the foregoing discussion, Dr. W. G. Brown has called the writer's attention to a further point which may be pertinent. Thermodynamic data on $Br_2$ and HBr[12b] indicate, according to Brown, that $Br_2$ has a low-energy excited level or levels, even lower than the low predicted ${}^3\Pi_{2u}$. Brown suggests that possibly the ${}^1\Pi_u$ is *lower* than the ${}^3\Pi_{1u}$ and ${}^3\Pi_{2u}$, giving far infrared bands. This, however, seems improbable, but the data in question nevertheless demand explanation.

## 9. The *D* level of $I_2$ and its analogues

Several investigators have studied an extensive set of $I_2$ absorption bands in the region surrounding λ2000.[13] It now appears very probable that these bands belong to a single upper electronic level,[14] called the *D* level. The *D* state, since it does not dissociate into two $5p$, ${}^2P$ atoms, probably gives the next lowest possible pair of dissociation products, *viz.*, one unexcited atom ($5p^5$, ${}^2P_{1\frac{1}{2}}$) and one excited atom[10, 13] ($5p^46s$, ${}^4P_{2\frac{1}{2}}$, with nearly *J–J* coupling). Van Vleck[4] has suggested that the *D* level may be a ${}^1\Sigma^+_u$. Several reasons can be advanced to support this suggestion.

In the first place, ${}^1\Sigma^+_u$ is a type of level which cannot dissociate into two $5p^5$, ${}^2P$ atoms. According to the ordinary Wigner-Witmer rules, ${}^2P+{}^2P$ gives no ${}^1\Sigma^+_u$ states. We cannot, however, rely entirely on these rules for $I_2$ but must use the modified rules appropriate to case *c*; in case *c*, ${}^1\Sigma^+_u$ is $0^+_u$. According to these rules,[1] only one $0^+_u$ state can result from ${}^2P+{}^2P$, and this is already known, it being the familiar low-energy ${}^3\Pi_{0^+u}$ state. Hence if the *D* level is ${}^1\Sigma^+_u$, or any other $0^+_u$, it cannot dissociate into two ${}^2P$ atoms.

We can now go further and tentatively identify the *D* state as the $\sigma_g\pi^4\pi^4\sigma^*_u$, ${}^1\Sigma^+_u$ given in (14) of section 5. According to the approximate $U(r)$ curve given by Curtis and Evans,[13] the vertical excitation energy of the *D* state is about 6.5 volts, while the *minimum* of its $U(r)$ is perhaps about 5.15 volts up.[14]

The *D* state is remarkable in that it has a very low $\omega_e$ (~100 as compared with 215 for the ground state),[14] and doubtless a correspondingly large $r_e$, yet has a dissociation energy larger than that of the ground state. The same peculiarities (wide flat $U(r)$ curve with large $r_e$ and large *D*) are found in the $1s\sigma 2p\sigma$, ${}^1\Sigma^+_u$ state of $H_2$ and in analogous states of $Li_2$, $Na_2$, etc.[15] This similarity, taken together with other reasons already noted, renders the argument for $\sigma_g\pi^4\pi^4\sigma^*_u$, ${}^1\Sigma^+_u$ very strong.

If we omit the closed shells of non-bonding electrons $\pi^4\pi^4$ in $I_2$, we have, for both $H_2$ and (cf. Table III) for $I_2$:

$$\left\{\begin{array}{l} \text{Normal states: } \sigma_g{}^2,\ {}^1\Sigma^+_g \\ \text{Peculiar } {}^1\Sigma^+_u \text{ and repulsive } {}^3\Sigma^+_u \text{ state:} \\ \hfill \sigma_g\sigma_u,\ {}^{1,\,3}\Sigma^+_u \\ \text{Also, } \sigma_u{}^2,\ {}^1\Sigma^+_g, \end{array}\right\}, \quad (18)$$

where $\sigma_g$, $\sigma_u=(1s\sigma\pm 1s\sigma)$ in the case of $H_2$, $(5p\sigma\pm 5p\sigma)$ in that of $I_2$.

In $H_2$ the vertical interval from the ${}^1\Sigma^+_g$ normal state ($r=r_e$) to the ${}^1\Sigma^+_u$ state is about 12 volts, in $I_2$ about 6.5 volts according to the present interpretation of the *D* state. In $H_2$ the explanation of the shape of the $U(r)$ curve of the ${}^1\Sigma^+_u$ has been given by Hund, Kemble and others, and is well known: two neutral H atoms each with a $1s$ electron may give either the ${}^1\Sigma^+_g$ attractive or the ${}^3\Sigma^+_u$ repulsive state (Heitler-London); two *ions* $H^++H^-(1s^2,\ {}^1S)$ tend to give the ${}^1\Sigma^+_u$ state or a second ${}^1\Sigma^+_g$ (cf. (18)). It is the essentially ionic character of the ${}^1\Sigma^+_u$ which causes its $U(r)$ curve at moderately large *r*

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[12b] W. G. Brown, J. Am. Chem. Soc. **54**, 2394 (1932); A. R. Gordon and C. Barnes, J. Chem. Phys. **1**, 692 (1933).

[13] Cf. W. E. Curtis and S. F. Evans, Proc. Roy. Soc. **A141**, 603 (1933), for a survey of the $I_2$ spectrum, with references to earlier work; also reference 10, Fig. 2, p. 610 shows an approximate $U(r)$ curve for the *D* state.

[14] D. T. Warren, Phys. Rev. **45**, 561 (1934), and private communications.

[15] Cf. e.g., R. S. Mulliken, Rev. Mod. Phys. **4**, 16 and 46 (1932).

values to resemble in shape that of two ions $H^+ + H^-$, while the presence of the anti-bonding electron $\sigma^*{}_u$ causes the curve to reach a minimum at large $r_e$.

The ${}^1\Sigma^+{}_u$ state of $H_2$ in (18) does not actually give two ions on dissociation, because to do so its $U(r)$ curve would have to cross several other ${}^1\Sigma^+{}_u$ curves derived from one normal plus one excited atom; actually it avoids such crossings and dissociates to give an atom in a 2-quantum state. For the $D$ state of $I_2$, an analogous explanation may well be accepted. Several workers[13] have suggested previously that it dissociates to $I^+ + I^-$, and this seems quite possible, but more probably it really dissociates to neutral atoms, one normal and one excited. The energy required to excite $2(5p^5,\ {}^2P_{1\frac{1}{2}})$ to produce $p^5,\ {}^2P_{1\frac{1}{2}} + p^4s,\ {}^4P_{2\frac{1}{2}}$ is 6.74 volts, to produce $I^- + I^+(p^4,\ {}^3P_2)$ is about 7.3 volts.[6]

With these points tentatively decided, we can predict that $I_2$ has a ${}^3\Sigma^+{}_u$ state, like $H_2$, with a $U(r)$ curve lying somewhat below that of the ${}^1\Sigma^+{}_u$ for small $r$ values, but probably giving two $np^5,\ {}^2P$ atoms on dissociation, like the normal state of the molecule. [There is a possibility, however, that the $1_u$ (case $c$) component of this ${}^3\Sigma^+{}_u$, in order to avoid crossing another $1_u$ curve (cf. Table III), gives $p^5,\ {}^2P + p^4s,\ {}^4P$ instead of $2(p^5,\ {}^2P)$ on dissociation.] Transitions from the normal state of $I_2$ to this ${}^3\Sigma^+{}_u$ state should give rise to a continuum [or possibly to discrete bands] in the ultraviolet with maximum intensity perhaps near λ2200. Strong absorption, apparently continuous, beginning at λ3700 or sooner, and increasing toward a maximum at λ2200 or below, is present in $I_2$ (also at shorter wave-lengths in $Br_2$) according to Coehn and Stuckardt.* Other authors, however, have reported only discrete bands in this region for $I_2$, but have reported continuous absorption for $Br_2$ and $Cl_2$.[9]

No absorption to a level analogous to the $D$ ${}^1\Sigma^+{}_u$ level of $I_2$ has been found in $Br_2$ or $Cl_2$, although the spectrum has been investigated down to λ1560 (equivalent to 7.9 volts).[9] This probably means that the $D$ levels of these molecules lie (vertically) higher than 8 volts above the normal level. This is not unreasonable, at least for $Cl_2$, since the interval between the normal state and the $D$ state would be expected to increase with decreasing atomic number. Continuous absorption, attributable presumably to transitions to $\sigma_g\sigma_u$, ${}^3\Sigma^+{}_u$ and some of the other highly repulsive $U(r)$ curves that the theory demands (cf. Table III) is present in this region, especially in $Br_2$, increasing in intensity toward shorter wave-lengths. In the case of $Br_2$, this might have obscured weak $D \leftarrow {}^1\Sigma^+{}_g$ bands which one would be inclined to expect near λ1600 or even at greater wave-lengths.

If the foregoing interpretation of the $D$ level of $I_2$ is correct, we have a means of determining approximately the $I$ (term value) of the orbital $(5p\sigma + 5p\sigma,\ \sigma_g)$ of $I_2$: cf. Table I, next-to-last line, together with footnote $f$ and last sentence of footnote $e$. The rough value $I = 14.3$ volts so obtained is in satisfactory agreement with that predicted in Table I ($I > 12.93$).

Taking $I = 14.3$ for the bonding $\sigma_g$ orbital of $I_2$, we can estimate $I$ for the bonding $\sigma$ orbital $(3p\sigma_{\mathrm{Cl}} + 5p\sigma_{\mathrm{I}})$ of ICl (cf. next to last paragraph of section 2). This should be considerably larger than for $\sigma_g$ of $I_2$, because the orbital is composed predominantly of $3p\sigma_{\mathrm{Cl}}$; 16.8 volts seems a reasonable estimate for it. Subtracting from this the estimated term value of $\sigma^* = (5p\sigma_{\mathrm{I}} - 3p\sigma_{\mathrm{Cl}})$ as given in Table I, we get 8.0 volts for $\sigma \to \sigma^*$ in ICl, the energy required to excite normal ICl to the state $\sigma\pi^4\pi^4\sigma^*$ (mean of ${}^3\Sigma^+$ and ${}^1\Sigma^+$) analogous to that of $I_2$ in (18). We then estimate 7.5 and 8.5 volts as the respective vertical excitation potentials of the ${}^3\Sigma^+$ and ${}^1\Sigma^+$. While these estimates are of course uncertain, they at least give a possible reason why no bands having an upper level analogous to $D$ of $I_2$ have yet been observed in ICl: they indicate that these bands should lie at shorter wave-lengths than the bands discussed in section 5, while the reverse is true in $I_2$. Similar relations are predicted in BrCl and IBr.

The probable predissociation observed by Cordes and Sponer in the states $\sigma^2\pi^4\pi^3\sigma^\times$ of ICl, IBr, and BrCl discussed in section 6 may now perhaps be attributed to crossing of their $U(r)$ curves by the $\pi^4\pi^4\sigma^*$, ${}^3\Sigma^+$ curve, or else by repulsive curves of the ${}^3\Sigma^+$ (or ${}^3\Delta$) states of the configuration $\sigma^2\pi^3\pi^3\sigma^{*2}$ (cf. Table IV).

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* Absorption of HI, HBr, $I_2$, $Br_2$, $Cl_2$ to λ2200, A. Coehn and K. Stuckardt, Zeits. f. physik. Chemie **91**, 737 (1916).

Table IV. *Predicted electronic states of ICl.*

| *Est. mean vert. energy*[a] | *Elec. Confign.* in terms of molecular orbitals; numbers of | | | | *Electron States* | | *Dissociation*[c] | | *Elec. Confign.* (atomic orbitals) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\sigma$ | $\pi$ | $\pi$ | $\sigma^*$ | Case *a*, *b*, or $\Omega$–*s* type | Case *c* type | products | energy | Cl | I |
| 16 | 0 | 4 | 4 | 2 | $^1\Sigma^+$ | $0^+$ | *ex* | | $3p\pi^4$ | $5p\sigma^2\ 5p\pi^4$ |
| 12.9 | 1 | 3 | 4 | 2 | $^{1,\,3}\Pi$ | $1, 0^-, 0^+, 1, 2$ | *ex* | | $\sigma\pi^3$ | $\sigma^2\pi^4$ |
| 10.4 | 1 | 4 | 3 | 2 | $^{1,\,3}\Pi$ | " | *ex* | | $\sigma^2\pi^4$ | $\sigma\pi^3$ |
| 9.8 | 2 | 2 | 4 | 2 | $^1\Sigma^+$, $^1\Delta$, $^3\Sigma^-$ | $0^+, 2, 1, 0^+$ | *ex* | | $\sigma^2\pi^2$ | $\sigma^2\pi^4$ |
| 8.0 | 1 | 4 | 4 | 1 | $^1\Sigma^+$ | $0^+$ | *ex* | | $\sigma^2\pi^4$ | $\pi^4$ |
| | | | | | $^3\Sigma^+$ | $\left\{\begin{matrix}1\\0^-\end{matrix}\right.$ | *bb**<br>*bb** | | $\sigma\pi^4$ | $\sigma\pi^4$ |
| 7.2 | 2 | 3 | 3 | 2 | $^1\Sigma^+$<br>$^1\Delta$<br>$^3\Sigma^-$<br>$^3\Sigma^+$<br>$^3\Delta$<br>$^1\Sigma^-$ | $0^+$<br>$2$<br>$\left\{\begin{matrix}0^+\\1\end{matrix}\right.$<br>$1, 0^-$<br>$\left\{\begin{matrix}1, 2\\3\end{matrix}\right.$<br>$0^-$ | *ex*<br>*ex*<br>*ex*<br>*ex*<br>*ba**<br>*ba**<br>*aa*†<br>*aa*** | 3.08 | $\sigma^2\pi^3$ | $\sigma^2\pi^3$ |
| 6.90 | 2 | 4 | 3 | $\sigma^\times$ | $\Pi$ | $\left\{\begin{matrix}0^-\\1, 0^+, 1, 2\end{matrix}\right.$ | *ex*<br>*ex** | 8.88 | $\sigma\pi^4$ | $\sigma\pi^3\ 6s$ |
| 4.9 | 2 | 3 | 4 | 1 | $^1\Pi$<br>$^3\Pi$ | $1$<br>$\left\{\begin{matrix}0^-\\0^+\\1, 2\end{matrix}\right.$ | *ab*<br>*ab***<br>*bb*<br>*aa*, *ab* | 3.19 | $\sigma^2\pi^3$ | $\sigma\pi^4$ |
| 4.8 | 2 | 4 | 2 | 2 | $^1\Sigma^+$<br>$^1\Delta$<br>$^3\Sigma^-$ | $0^+$<br>$2$<br>$1, 0^+$ | *aa****<br>*aa*<br>*ab*, *ba* | | $\sigma^2\pi^4$ | $\sigma^2\pi^2$ |
| 2.4 | 2 | 4 | 3 | 1 | $^1\Pi$<br>$^3\Pi$ | $1$<br>$\left\{\begin{matrix}0^+\\0^-, 1, 2\end{matrix}\right.$ | *aa*<br>*ab****<br>*aa* | 2.25 | $\sigma\pi^4$ | $\sigma^2\pi^3$ |
| 0.00 | 2 | 4 | 4 | 0 | $^1\Sigma^+$ | $0^+$ | *aa* | 2.14 | $\sigma\pi^4$ | $\sigma\pi^4$ |

*Notes for Table IV* (*cf. also Table III notes*). [a] Cf. note *a* of Table III. Estimated mean energies based on: $\pi_\mathrm{I}\rightarrow\sigma^*$, 2.4 volts, from visible bands (cf. Table I); $\pi_\mathrm{Cl}\rightarrow\pi_\mathrm{I}$, 2.5 volts, from difference between $I^*_\mathrm{Cl}$ and $I^*_\mathrm{I}$ (cf. Table I); $\sigma\rightarrow\sigma^*$, 8.0 volts, rough (cf. Table I, and its note **f**); $\pi_\mathrm{I}\rightarrow\sigma^\times$, from vacuum ultraviolet bands. [c] *aa*, *ab*, *ba*, *bb* mean ${}^2P_{1\frac{1}{2}}+{}^2P_{1\frac{1}{2}}$, ${}^2P_{1\frac{1}{2}}(\mathrm{I})+{}^2P_{\frac{1}{2}}(\mathrm{Cl})$, ${}^2P_{\frac{1}{2}}(\mathrm{I})+{}^2P_{1\frac{1}{2}}(\mathrm{Cl})$, ${}^2P_{\frac{1}{2}}+{}^2P_{\frac{1}{2}}$. The one "unique state" is marked with a dagger. Cf. Table III, footnote *c* in regard to uncertainties in dissociation products. These are greater here than for $I_2$, because of the loss of the $_g$, $_u$, classification.

## 10. Ultraviolet fluorescence and emission spectra of $I_2$

When $I_2$ absorbs light in the region of the $D\leftarrow{}^1\Sigma^+_g$ bands, a complicated fluorescence spectrum is obtained, which has been studied by McLennan, Oldenberg and others.[13] The short wave-length end of this is a series of sharp lines (or narrow groups of lines) representing transitions from the initial rotational and vibrational level (or levels) of the $D$ state produced by the absorption act to various levels of the $^1\Sigma^+_g$ normal state of the molecule. At longer wave-lengths are numerous diffuse bands. This part of the fluorescence spectrum is independent of the exciting wave-length over a wide range of the latter. Oldenberg[13] suggests that it results from the occurrence of two (or more) sets of transitions in succession, the first from the $D_u$ level to vibrational levels of an unknown electron level, say $X_g$, slightly below $D$, the second from $X_g$ vibrational levels to a lower electron state $Y_u$. There might of course be more than one $X_g$ or $Y_u$. The transitions $D_u\rightarrow X_g$ might be in the infrared, Oldenberg suggests.

The emission spectrum of iodine[13, 16] at low pressures shows part of the fluorescence bands. At high pressures additional sets of bands appear, some of which are also developed in fluorescence under high pressures of foreign gas. Some $F_2$, $Br_2$ and $Cl_2$ emission bands are also known,[16, 12] and deserve further investigation.

No attempt will be made here to offer a detailed explanation of the fluorescence and emission spectra of the halogens. One finds, however, on applying the method of electron configurations, that the $I_2$ molecule must possess a surprisingly large number of hitherto unknown low-energy states, some $_g$ and some $_u$, theoretically derivable by bringing together two $5p^5$, $^2P$ I atoms or $I^+(5p^4)+I^-(5p^6, {}^1S)$. These are given, with rough estimates of their energy, in Table III. Most of the lower-energy ones among these states should be of repulsive type, giving two $5p^5$, $^2P$ I atoms on dissociation. Two groups of states, however, one $_u$ and one $_g$, estimated to lie in the energy range 5–6 volts, and having wave functions of nearly ionic character $(I^+I^-)$, must dissociate to give an excited I atom (or $I^+ + I^-$), and must be stable states, although all should have the minima of their $U(r)$ curves at very large $r$ values. One of these predicted states is of type $^1\Sigma^+{}_g$ and its estimated position is right for the postulated level $X_g$. This and some of the other predicted states offer promising possibilities for explaining the various observed $I_2$ emission bands. It should, however, be pointed out that while the *existence* of the states listed in Table III is inescapable according to the theory, the estimates of their energies given there are to a considerable extent only enlightened guesswork. It should also be emphasized that the energy estimates given refer to *vertical* excitation energies; the course of the $U(r)$ curves is not estimated except insofar as this is determined from the vertical energy together with the dissociation products (cf. Table III, notes, second paragraph). It may also be well to mention that, from about 7 volts up, there should appear innumerable additional electronic states derivable from atoms or ions in which one or more electrons are in excited orbits.

Among the as yet unknown excited states of $I_2$ predicted in Table III, the $^3\Pi_g$ and $^1\Pi_g$ states given by (13) are of considerable interest. As we have seen in section 5, they should lie only a little above, or perhaps in part overlapping, the $^{1,\,3}\Pi_u$ states of (12), whose $^3\Pi_{0^+u}$ and $^3\Pi_{1u}$ are the upper levels of the known visible and infrared absorption bands. Like the $^{3,\,1}\Pi_u$, they should show $\Omega$–$s$ coupling, so that the triplet, singlet labels are really not apt. The case $c$ dissociation rules[1] make it probable that the $^3\Pi_{2g}$, $^3\Pi_{1g}$, and $^3\Pi_{0^+g}$ dissociate into unexcited atoms (both $^2P_{1\frac{1}{2}}$) and so are repulsive, but show that the $^3\Pi_{0^-g}$ and $^1\Pi_g$ must give one excited atom on dissociation, so that the $U(r)$ curve of $^3\Pi_{0^-g}$, and of $^1\Pi_g$, may have a shallow minimum. Absorption transitions to these states $^{3,\,1}\Pi_g$ are of course forbidden by the $g \longleftrightarrow u$ selection rule. Emission transitions from the $D_u$ state to the $^1\Pi_g$ should occur; also, to the $^3\Pi_{1g}$ and $^3\Pi_{0^+g}$. Transitions to the last-named should be strong if the strong mutual perturbation between it and the normal state, suggested in section 7, exists.

## 11. Middle ultraviolet absorption continua of ICl, IBr, BrCl; fluorescence of IBr

Just as in $I_2$, so in ICl there should exist a large number of hitherto unknown or little known low-energy excited states, most of them unstable (repulsive) because dissociating to $I(5p^5, {}^2P)+Cl(3p^5, {}^2P)$. Others, higher up, should be stable, because giving a strongly excited atom on dissociation. The predicted states theoretically derivable by bringing together $I(p^5, {}^2P)+Cl(p^5, {}^2P)$, $I^+(p^4)+Cl^-(p^6, {}^1S)$, or $I^-(p^6, {}^1S)+Cl^+(p^4)$ are shown, with rough estimates of their energies, in Table IV. Of especial interest are the $\sigma^2\pi_{Cl}{}^3\pi_I{}^4\sigma^*$, $^3\Pi$ and $^1\Pi$. These (cf. (13)) are analogous to the $^{1,\,3}\Pi_g$ of $I_2$ just discussed. They differ from the latter in two important respects: (1) absorption transitions to them from the normal state of the molecule are now to be expected, since there is no longer any $g \longleftrightarrow u$ selection rule; (2) the interval between the $^{1,\,3}\Pi$ of (12) and the $^{1,\,3}\Pi$ of (13) should probably (see below) be very considerably larger than the corresponding interval for $I_2$ ($^{1,\,3}\Pi_g$

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[16] R. J. Strutt and A. Fowler, Proc. Roy. Soc. **A86**, 105 (1911): excitation of $Cl_2$, $Br_2$, and especially $I_2$ emission bands in active nitrogen. This interesting work, containing extensive data and an excellent photograph of the $I_2$ band spectrum, seems to be generally overlooked. Cf. also reference 8 ($X_2^+$? or perhaps $X_2$ emission bands).

$-^{1,3}\Pi_u$) and, as a result, the $^{1,3}\Pi$ of (13) should be entirely repulsive for ICl, so that the absorption spectrum for transitions to them from the normal state should be continuous. Also, (**3**), since the $^{1,3}\Pi$ of (13) correspond to excitation of a Cl $\pi$ electron, the multiplet width should correspond to that of the Cl atom, instead of to that of the I atom as in (12); as a result of this, the coupling should tend more toward the $\Lambda-\Sigma$ rather than the $\Omega-s$ type.

The energy interval $\Delta\Pi$ between $^{1,3}\Pi$ of (12) and of (13) would be expected to be approximately equal to the interval $(\Delta\Pi)^+$ between the two low-energy $^2\Pi$ states of the molecule-ion (cf. (7), (8) for ICl, (9), (10) for $I_2$), since (12) and (13) are, respectively, obtainable by the addition of a $\sigma^*$ electron to (7) or (9) and (8) or (10), respectively. As we have seen in section 4, $(\Delta\Pi)^+$ is probably not large for $I_2$, while for ICl it should be approximately equal to the difference between the $\pi_{\text{Cl}}$ and $\pi_{\text{I}}$ ionization of type $I^*$, namely, 2.5 volts (cf. Table I).

As we have seen in the last paragraph of section 8, the ICl transitions $^{1,3}\Pi \leftarrow {}^1\Sigma^+$ to the $^{1,3}\Pi$ of (12) consist of bands accompanied by a continuum, whose maximum is at about λ4700. In the analogous cases of IBr, BrCl, the maximum of the continuum is at λ4950, λ3750, respectively. It seems safe in these cases to take the continuum-maxima as giving roughly the mean vertical excitation energy of the $^{1,3}\Pi$ of (12). Now there is in the ultraviolet spectrum of each of the above three molecules, according to Cordes and Sponer,[9, 3] one (and only one) additional strong continuum in the region between the above-mentioned continua and λ2000. The second continuum has its maximum at λ2400 for ICl, λ4050 for IBr, λ2150 for BrCl.

It seems very reasonable to identify the second continuum in each case as corresponding to transitions from the normal state of the molecule to the predicted higher-energy $^{1,3}\Pi$ given by (13). According to our discussion in a preceding paragraph, the frequency interval between the maxima of the two continua may then be called $\Delta\Pi$ and should be roughly equal to the interval $(\Delta\Pi)^+$ of the molecule-ion. In Table V, the $\Delta\Pi$ and estimated $(\Delta\Pi)^+$ are compared. The agreement is good enough, in view of the necessary neglect of various modifying factors, theoretical as well as perhaps also experimental, to give strong support to our explanation of the second continua.

TABLE V. *Frequency intervals (volts).*

| | ΔΠ(obsd.) | (ΔΠ)⁺(est.) |
|---|---|---|
| ICl | 2.52 | 2.50 |
| IBr | 0.55 | 1.27 |
| BrCl | 2.45 | 1.23 |

*Note:* The $(\Delta\Pi)^+$ values are obtained by taking $I^*_{\text{Y}} - I^*_{\text{X}}$ from Table I. The $\Delta\Pi$ for BrCl is based on an observed maximum at λ3700 or 3800 for BrCl dissolved in $CCl_4$ and on a second maximum at λ2150 in the vapor.

A reasonable interpretation can now be given for the $U(r)$ curve of $0^+$ type which was found, by Brown and Gibson[3] in ICl and by Brown[3] in IBr, to cross the $U(r)$ curve of the $^3\Pi_{0^+}$ state belonging to the lower-energy $^{1,3}\Pi$ group. This second $0^+$ curve (cf. also discussion by Cordes and Sponer[9]) may reasonably be identified as belonging to the $^3\Pi_{0^+}$ component of the higher-energy $^{1,3}\Pi$ group,—in agreement with the suggestions of Brown and Gibson and of Brown that this $0^+$ curve might be the cause of the λ2400 continuum in ICl and of the λ4050 continuum in IBr.

An analogous explanation should apply to the similar $0^+$ curve of IBr, reported by Brown (cf. Van Vleck,[4] footnote 23).

If Table IV for ICl is approximately correct in regard to the energies of various states, a group of states ($^1\Sigma^+$, $^1\Delta$, $^3\Sigma^-$) belonging to $\sigma^2\pi_{\text{Cl}}{}^4\Pi_{\text{I}}{}^2\sigma^{*2}$ should exist at about the same energy as the $\sigma^2\pi^3\pi^4\sigma^*$, $^{1,3}\Pi$ just discussed; and transitions to the $^1\Sigma^+$ and the $^3\Sigma^-$ from the normal state of ICl should occur. These might contribute to the λ2400 continuum of ICl. It seems likely, however, that this contribution is relative very weak since transition to $\sigma^2\pi^4\pi^2\sigma^{*2}$ from $\sigma^2\pi^4\pi^4$ (normal state) would mean a two-electron jump.

No other low-energy levels of ICl are predicted in Table IV below the neighborhood of $\sigma^2\pi^4\pi^3\sigma^\times$ (upper level of the bands discussed in section 6). Further discussion of the predicted levels of $I_2$ and ICl in Tables III and IV, and of analogous but energetically different levels in the other halogens, is unnecessary. From the electron configurations and states, their estimated energies, selection rules, likely weakness of many not-forbidden transitions (especially, perhaps, two-electron jumps), etc., readers can draw their own conclusions.

The ultraviolet fluorescence spectrum of $I_2$ which follows excitation to the $D$ electron level has already been discussed. No similar spectrum has been found in any of the other halogens $X_2$ or XY, except in IBr.[17] The IBr fluorescence resembles that of $I_2$, except that it does not follow excitation to the $D$ state of IBr, which is not yet known (cf. end of section 9), but presumably (cf. Cordes[3]) to energy levels belonging to $\sigma^2\pi^4\pi^3\sigma^\times$, $\Pi$ (cf. section 6).

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[17] F. W. Loomis and A. J. Allen, Phys. Rev. **33**, 639 (1929) obtained IBr and $I_2$ fluorescence by λ1849 excitation, but obtained none in $Br_2$, ICl, or BrCl.

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# Rotational and Vibrational Structure of the Fourth Positive Bands of Carbon Monoxide

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The rotational structure of twelve of the fourth positive bands of CO ($A\,^1\Pi-X\,^1\Sigma$) has been measured and analyzed. The analyses of two bands are given. The values obtained for the rotational constants of the normal state are $B_0=1.9170$ cm$^{-1}$, $\alpha=0.01738$ cm$^{-1}$. This is in disagreement with the result of infrared band measurements, which give $B_0=1.84$. The data obtained on the excited $A\,^1\Pi$ state are in complete agreement with the results of Angstrom ($B\,^1\Sigma-A\,^1\Pi$) band studies. The higher value of $B_0$ for the normal state is verified by measurement of the $0-0$ band of the ultraviolet system $B\,^1\Sigma-X\,^1\Sigma$. The recently reported predissociation of the $B$ state is also observed in this band. New measurements are given of the fourth positive band heads below 2270A. A formula is given to represent all the known band heads, and from this a formula for band origins is obtained.

## Introduction

THE carbon monoxide spectrum is one of the most exhaustively studied of all molecular spectra. Nevertheless, no rotational analyses have been reported of bands involving the normal state of the molecule. Most of these lie in the far ultraviolet region.

The most important of the ultraviolet band systems is the fourth positive ($A\,^1\Pi-X\,^1\Sigma$). About 140 band heads have been identified, extending from about 1300 to 2600A. The upper state of this system is the lower state of the well-known Angstrom band system ($B\,^1\Sigma-A\,^1\Pi$). The vibrational analysis is given by Birge,[1] and more recent band head measurements have been reported by Headrick and Fox,[2] and by Estey.[3] The object of this paper is to report rotational analyses of a number of these bands, and more accurate band head measurements.

## Experimental

The present work is based on a spectrogram taken by Professor H. D. Smyth with the two-meter vacuum spectrograph at Massachusetts Institute of Technology.[4] The source used was a hollow cathode discharge in flowing $CO_2$. The original object was to search for $CO_2$ emission bands, but none were found in this region.

The plate covers the region from 0 to about 2475A with a dispersion of 4.2A/mm. It shows about 65 heads of the fourth positive system of CO. Many of the bands are quite intense and well resolved except in the immediate neighborhood of the heads. There are also present on the plate a number of the first negative bands of $CO^+$, six of the ultraviolet bands of CO reported by Hopfield and Birge,[5] and atomic lines due to C, O, N, and Ni.

The measurements of the plate were converted to wave-lengths by use of a dispersion table for

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[1] Birge, Phys. Rev. **28**, 1157 (1926).

[2] Headrick and Fox, Phys. Rev. **35**, 1033 (1930).

[3] Estey, Phys. Rev. **35**, 309 (1930).

[4] Compton and Boyce, Rev. Sci. Inst. **5**, 218 (1934).

[5] Hopfield and Birge, Phys. Rev. **29**, 922 (1927).