acceptable value of b, for one of the suggested closed universes, it would be necessary to look upon the electron as being usually in a very high state, $N\sim 10^{37}$, of the elementary particle, whose lowest mass state would be $m\sim 10^{-65}$ g.

We must keep in mind, however, that these interpretations are based upon the tacit assumption that Dirac's equation is correct for all distances. It is one of those cases in which success would be very gratifying, but the failure is not surprising. Of course, since the only dimensional constants occurring in the equations are h, m, and c, the mass of the electron and the radius of the universe b can be connected only by a relation such as Eq. (6.24) with N a large dimensionless number. The fact that the theory fails to supply any such number shows that Dirac's equation does not provide a model capable of explaining the mass of the electron in terms of the radius of the universe, which is perhaps not surprising.

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Halogen Molecule Spectra

II. Interval Relations and Relative Intensities in the Long Wave-Length Spectra

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Quantum-theoretical expressions are obtained in Section II for energy-intervals among the levels belonging to related $^3\Pi$ and $^1\Pi$ states of any diatomic molecule, for partial Ω,ω (J,j-like) coupling. A theoretical expression is also obtained for the relative intensities of spectroscopic transitions from a $^1\Sigma$ to the $^3\Pi_1$ and $^1\Pi$ states. The effect of partial case c coupling (persistence of separate-atom J quantization) on the foregoing relations is studied in Section III. Equations are obtained which (together with equations of Van Vleck) permit computation of case c displacements of certain energy levels of the halogen molecules. The foregoing relations are applied in Sections IV and V to a refinement of the existing interpretations of the long wave-length absorption spectra of the diatomic halogen molecules (cf. Tables II, III). In the case of bromine, it is found impossible to decide between two alternative interpretations; suggestions are made for further work that could lead to a decision. Information is obtained bearing on the strength of the dissociation continuum overlying the bands in Cl_2, Br_2, and I_2, on the positions of the $^1\Pi$ and $^3\Pi_{0^-u}$ potential energy curves in I_2 and on the cause of magnetic predissociation in I_2. The desirability of quantitative measurement of the infra-red continuum of iodine and careful remeasurement of the visible continuum of iodine chloride are mentioned. Two mechanisms (proposed by Van Vleck and the writer) for explaining the remarkably high intensity of the $^1\Sigma\rightarrow{}^3\Pi_{0^+}$ component in the halogen spectra are examined in Section VI. Both give calculated intensities approaching the observed in order of magnitude. The weak λ2250 bromine continuum is discussed in Section VIII; its occurrence and intensity seem to be explainable by a case-c-allowed intersystem combination.

I. INTRODUCTION

THE present paper and one appearing simultaneously[1] have to do with intensity relations in the absorption spectra of the halogen molecules. In the present paper, which represents a continuation of previous studies,[2, 3] we shall be mainly concerned with the longest wave-length regions of the absorption spectra of F_2, Cl_2, Br_2, and I_2. These occupy the near infra-red and the visible, or extend into the ultraviolet for the lighter molecules. The spectra consist partly of discrete bands, partly of continuous absorption, but the ensemble in each case belongs[2-4] to a single group of electronic transitions. These all arise from the normal state of the molecule (N)

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[1] R. S. Mulliken, J. Chem. Phys. **8**, 234 (1940).

[2] The paper by R. S. Mulliken, Phys. Rev. **46**, 549 (1934) may be regarded as I. Earlier papers on the same subject are referred to there. See Phys. Rev. **51**, 311 (1936) footnote 4, also p. 314 for a correction. The quantity $G'D$ of reference 8 and the present paper is identical with the square of the quantity P/e of the 1934 paper.

[3] R. S. Mulliken, J. Chem. Phys. **4**, 620 (1936).

[4] Bromine: N. S. Bayliss *et al.* J. Chem. Phys. **7**, 854 (1939), and references given there. Chlorine: R. G. Aickin and N. S. Bayliss, Trans. Faraday Soc. **33**, 1333 (1937).

and go to certain excited electronic states which may for simplicity be called the Q states.[5] For brevity, we may in the following speak of this group of states as the "*Q complex*," and of the group of $N\rightarrow Q$ transitions as the "*$N\rightarrow Q$ complex*."

N is a $^1\Sigma^+_g$ state, and the Q complex consists of the multiplet components of a $^3\Pi_u$ state ("^3Q"), together with the corresponding $^1\Pi_u$ state ("^1Q"). The Q states belong to an electron configuration $\cdots\sigma_g{}^2\pi_u{}^4\pi_g{}^3\sigma_u$ in terms of molecular orbitals; or $\sigma\pi^4\cdot\sigma^2\pi^3$ in terms of atomic orbitals. In either case, it is the interaction between a σ electron and a π^3 group which is responsible for the occurrence of a triplet and a singlet Π state.

Of the components $^3\Pi_2$, $^3\Pi_1$, and $^3\Pi_0$ (itself divided into $^3\Pi_{0^+}$ and $^3\Pi_{0^-}$) of the ^3Q state, only $^3\Pi_1$ and $^3\Pi_0$ ("$^3Q_1$" and "Q_0") receive transitions from state N. This is because of the selection rule $\Delta\Omega=0, \pm1$, which is applicable in intersystem transitions when the spin coupling is tight.[2] Hence the $N\rightarrow Q$ complex should consist of the three transitions $N\rightarrow{}^3Q_1$, $N\rightarrow Q_0$ and $N\rightarrow{}^1Q$.

The relative intensities and other characteristics of these vary in an interesting way from F_2 to I_2. Hitherto, only qualitative theoretical considerations have been used[2-4] in apportioning the observed spectra to the three transitions. In Sections II and III of the present paper, theoretical expressions for the ratio of the intensity of $N\rightarrow{}^3Q_1$ to that of $N\rightarrow{}^1Q$, and for the energy intervals among the several Q levels, are developed. In the subsequent sections they are applied. This makes possible a more definite and reliable interpretation of the observed spectra. In a separate paper,[1] quantum-mechanical calculations are made for the sum of the absolute intensities of $N\rightarrow{}^3Q_1$ and $N\rightarrow{}^1Q$, and compared with the results of the present analysis.

II. THEORY NEGLECTING PERSISTENCE OF ATOMIC *J* QUANTIZATION

In the halogen molecule electronic levels, the coupling is for the most part intermediate between the Λ,S and Ω,ω types, but has strong tendencies (especially in the heavier halogens) toward separate-atom case c coupling, i.e., persistence of atomic J quantization.[2] Λ,S and Ω,ω coupling in diatomic molecules are the analogs of L,S and J,j coupling in atoms.* In the present section theoretical formulas are first obtained for the relative energies of the members of the Q complex of energy levels for the general intermediate case between Λ,S and Ω,ω coupling, neglecting case c tendencies and other secondary effects. The theoretical relative intensities of the members of the $N\rightarrow Q$ complex of transitions are then determined. Modifications of the theory to allow for case c influences are developed in Section III.

In Λ,S coupling (multiplet width small compared with the singlet-triplet separation X), the energies of the $^3\Pi$ and $^1\Pi$ states of an electron configuration $\sigma\pi$ or $\pi^3\sigma$ are well known to be

$$\begin{aligned} {}^1\Pi:&\quad E=E_0+X/2,\\ {}^3\Pi_0:&\quad E=E_0-X/2\pm a/2,\\ {}^3\Pi_1:&\quad E=E_0-X/2,\\ {}^3\Pi_2:&\quad E=E_0-X/2\mp a/2.\end{aligned} \tag{1}$$

The upper sign in $\pm$ or $\mp$ refers to $\pi^3\sigma$, the lower to $\pi\sigma$. We are interested *here* in $\pi^3\sigma$ $^{1,3}Q$ states, but the very similar case $\pi\sigma$ is also considered for the sake of generality. The symbols π and σ may be understood to refer either to AO's (atomic orbitals) or to MO's (molecular orbitals). The quantity a is the spin-orbit coupling coefficient for a single π electron, in the expression

$$E_{\text{spin-orbit}}=\sum_i a_i \mathbf{l}_i\cdot\mathbf{s}_i+\cdots. \tag{2}$$

In ideal Ω,ω coupling* we have a core (π^3 or π) within which there is tight spin-orbit coupling, plus an outer (here σ) electron. Ideal Ω,ω coupling would exist if $a\gg X$. In this ideal case, neglecting X, we have for $\pi^3\sigma$,

$$^1\Pi,{}^3\Pi_0: E=E_0+a/2,\quad {}^3\Pi_1,{}^3\Pi_2: E=E_0-a/2, \tag{3}$$

and for $\pi\sigma$,

$$^1\Pi,{}^3\Pi_2: E=E_0+a/2,\quad {}^3\Pi_1,{}^3\Pi_0: E=E_0-a/2. \tag{4}$$

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[5] Cf. R. S. Mulliken, Phys. Rev. 50, 1017 (1936).

* In reference 1, the name "Ω,s coupling" was introduced for a case in which the spin of a single outer σ electron is coupled to the Ω of a π^3 molecule-core. This case is similar to that of a rare gas atom with configuration $np^5(n+1)s$, where the spin of the excited electron is coupled to the J of the atom-core. This atomic case might reasonably be referred to as "J,S coupling" (S for spin). Ordinarily, however, one speaks of j,j or J,j or J,J coupling. Similarly in the diatomic case, we may well in general speak of ω,ω or Ω,ω, or Ω,Ω coupling.

(In ideal or approximate Ω,ω coupling, the singlet and triplet notation is of course no longer appropriate, but may be retained for convenience.)

The behavior of the several Π levels of the configuration $\pi^3\sigma$ as we go over from Λ,S to Ω,ω coupling is similar to that of the P levels of an atom of configuration p^5s as we go from L,S to J,j coupling. In first approximation, the wave functions and the energy for $^3\Pi_0$ and $^3\Pi_2$ of the molecule remain invariant throughout the whole range of changing coupling, just as do those of $^3P_2$ of the atom. Hence Eqs. (1) for $^3\Pi_0$ and $^3\Pi_2$ are valid independently of the coupling, provided we neglect case c and other secondary perturbing effects (of Section III). For $^3\Pi_1$ and $^1\Pi$, however, just as for $^3P_1$ and ^1P of the atom, increase in the ratio a/X brings about a gradual mixing of the singlet and triplet wave functions, with corresponding changes in the energy expressions, and in the relative strength of intersystem transitions.

The theoretical treatment is similar to Houston's treatment of the interaction between the atomic states $^3P_1$ and ^1P of p^5s or sp. In the general intermediate case between Λ,S and Ω,ω coupling, we shall have two wave functions

$$\begin{aligned}\psi(^3\Pi_1)&=\alpha\psi_0(^3\Pi_1)+\beta\psi_0(^1\Pi),\\ \psi(^1\Pi)&=\gamma\psi_0(^3\Pi_1)+\delta\psi_0(^1\Pi),\end{aligned}\qquad(5)$$

where $\psi_0(^3\Pi_1)$ and $\psi_0(^1\Pi)$ are "unperturbed" wave functions corresponding to Λ,S coupling. (Each of our wave functions is of course twofold degenerate.) In Eqs. (5), $\alpha^2+\beta^2=\gamma^2+\delta^2=1, |\alpha|>|\beta|, |\delta|>|\gamma|$. In the limit of ideal Ω,ω coupling, $|\alpha|=|\beta|=|\gamma|=|\delta|=2^{-\frac{1}{2}}$.

Setting up in the usual way the perturbation problem for the interaction of $\psi_0(^3\Pi_1)$ with $\psi_0(^1\Pi)$, we obtain the secular equation

$$\begin{vmatrix}H_{11}-E & H_{12}\\ H_{12} & H_{22}-E\end{vmatrix}=\begin{vmatrix}E_0-\frac{1}{2}X-E & \frac{1}{2}a\lambda\\ \frac{1}{2}a\lambda & E_0+\frac{1}{2}X-E\end{vmatrix}=0.\qquad(6)$$

The second form of the determinant is obtained by evaluating the H_{kl}'s:

$$H_{kl}=\int\psi_{0k}{}^*H\psi_{0l}d\tau,$$

with $H=H^0+\sum_i a_i\mathbf{l}_i\cdot\mathbf{s}_i$ (cf. Eq. (2)), with the spin-orbit terms expressed in proper operator form.[6] Introducing suitable antisymmetrical AO or MO wave functions for $\psi_0(^3\Pi_1)$ and $\psi_0(^1\Pi)$, we find that only the H^0 operator contributes to H_{11} and H_{22}, only the spin-orbit operator to H_{12}. The appropriate AO wave functions are given in reference 13, and the corresponding MO functions are easily constructed; both yield the same results $H_{11}=E_0-\frac{1}{2}X$, $H_{22}=E_0+\frac{1}{2}X$, $H_{12}=\frac{1}{2}a\lambda$, where $\lambda=+1$ or -1 according to the sign of the angular momentum of the π orbital in $\pi\sigma$, or of the *unpaired* π orbital in $\pi^3\sigma$. In the case of $\pi^3\sigma$, λ is opposite in sign to Ω, where $\Omega=\pm1$ represents the angular momentum of the total state (in $h/2\pi$ units). The solutions of Eq. (6) are:

$$E=E_0\pm\tfrac{1}{2}(X^2+a^2)^{\frac{1}{2}}.\qquad(7)$$

To check the result that $|H_{12}|=\frac{1}{2}a$, note that when $X=0$, Eq. (7) yields $E=E_0\pm\frac{1}{2}a$, in agreement with Eqs. (3).

In analogy to recent conclusions of King and Van Vleck in a study of observed s^2, $^1S\rightarrow sp$, $^3P_1$ and ^1P intensities and $^3P,^1P$ energy spacings in atoms,[7] it appears that in the equation $H_{12}=\pm a/2$, a factor μ somewhat less than 1 should be introduced, so that

$$H_{12}=\pm\mu a/2;\qquad(8)$$

μ should approach 1 if X approaches 0.

It is useful to introduce the parameter R:

$$R=X/\mu a.\qquad(9)$$

Using Eqs. (1) for $^3\Pi_2$ and $^3\Pi_0$, and Eq. (7), modified in accordance with Eq. (8), for $^3\Pi_1$ and $^1\Pi$, we have

$$\begin{aligned}E(^3\Pi_2,\,^3\Pi_0)&=E_0-\tfrac{1}{2}X(1\pm1/\mu R)\\ &=E_0\mp\tfrac{1}{2}a(1\pm\mu R),\\ E(^3\Pi_1,\,^1\Pi)&=E_0\mp\tfrac{1}{2}X(1+1/R^2)^{\frac{1}{2}}\\ &=E_0\mp\tfrac{1}{2}a\mu(1+R^2)^{\frac{1}{2}}.\end{aligned}\qquad(10)$$

For the configuration $\pi^3\sigma$, the $^3\Pi$ is *inverted*, and the upper signs in the first line of Eqs. (10)

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[6] Cf. e.g., J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), pp. 159–162, Eqs. (75), (78), (79).

[7] G. W. King and J. H. Van Vleck, Phys. Rev. **56**, 464 (1939).

belong to $^3\Pi_2$, the lower to $^3\Pi_0$. For $\pi\sigma$, the $^3\Pi$ is *regular*, and the choice of signs is reversed. For *either* configuration, the upper signs in the second line of Eqs. (10) belong to the $^3\Pi_1$, the lower to the $^1\Pi$ level.

Equations (10) neglect "case c tendencies" and other secondary effects. These should produce more or less distortion of the energy intervals and a splitting of the $^3\Pi_0$, especially for the heavier halogens (see Section III).

The following energy interval formulas based on Eqs. (10) will prove convenient:

$$\begin{aligned}\Delta\nu\equiv E(^1\Pi)-E(^3\Pi_1)&\\ =X(1+1/R^2)^{\frac{1}{2}}&=a\mu(1+R^2)^{\frac{1}{2}},\\ E(^1\Pi)-E(^3\Pi_0)&=\tfrac{1}{2}\Delta\nu+\tfrac{1}{2}a(\mu R-1),\\ E(^3\Pi_0)-E(^3\Pi_1)&=\tfrac{1}{2}\Delta\nu-\tfrac{1}{2}a(\mu R-1).\end{aligned}\qquad(11)$$

The last two equations apply only for *inverted* $^3\Pi$, as in the halogen Q states.

We now turn to the *intensities* of the three allowed transitions of the $N\rightarrow Q$ complex. In Λ,S coupling ($R=\infty$ in Eq. (9)), only $N\rightarrow{}^1\Pi$ would occur. As we go toward Ω,ω coupling, $N\rightarrow{}^3\Pi_1$ gradually steals intensity from $N\rightarrow{}^1\Pi$ until for ideal Ω,ω coupling ($R=0$) the intensity is equally divided between the two. This is because of the gradual mixing of the $\psi_0(^3\Pi_1)$ and $\psi_0(^1\Pi)$ functions (cf. Eqs. (5)).

The coefficients in Eqs. (5) are found to be as follows (cf. Section III):

$$\begin{aligned}\psi(^3\Pi_1)&=(1+z^2)^{-\frac{1}{2}}[z\psi_0(^3\Pi_1)+\psi_0(^1\Pi)],\\ \psi(^1\Pi)&=(1+z^2)^{-\frac{1}{2}}[\psi_0(^3\Pi_1)-z\psi_0(^1\Pi)],\end{aligned}\qquad(12)$$

or else with the sign of $\psi_0(^1\Pi)$ reversed in each equation (for our present purposes this does not matter). In Eqs. (12),

$$z=R+(R^2+1)^{\frac{1}{2}}.\qquad(13)$$

Each of the wave functions in Eqs. (12) is, as already noted, doubly degenerate. If we let x and y be two directions perpendicular to the axis of the molecule, and if we now use real wave functions, then the degenerate pairs of wave functions may be called $\psi(^3\Pi_{1x})$, $\psi(^3\Pi_{1y})$, and so on.

Now let D_1 be the *dipole strength* of the transition $N\rightarrow{}^3\Pi_1$, D_2 the same for $N\rightarrow{}^1\Pi$. In terms of experimental quantities, for either D_1 or D_2,

$$G'D=[3hc/8\pi^3ne^2]\int k_\nu d\nu/\nu$$
$$=3.83\times10^{-19}\int k_\nu d\nu/\nu,\qquad(14)$$

where k is the absorption coefficient, per cm, for gas or vapor corrected to 0°C. and 1 atmosphere pressure.[8] In the present case, $G'=2$, corresponding to the twofold degeneracy of $^3\Pi_1$ and $^1\Pi$. In Eq. (14), $G'D$ is in cm^2. A more convenient unit is the square angstrom; then

$$G'D=3.83\times10^{-3}\int k_\nu d\nu/\nu.\qquad(15)$$

In terms of quantum-mechanical theory,[8,*]

$$D=Q_x{}^2=Q_y{}^2,\quad Q_y=\int\psi(N)\Sigma y_i\psi(\Pi_{1y})dv,\qquad(16)$$

where $-e$ times Σy_i is the dipole moment operator for the y direction, and Π_{1y} stands for $^3\Pi_{1y}$ or $^1\Pi_y$.

Substituting from Eqs. (12) in Eq. (16), noting that

$$\int\psi^*(N)\Sigma y_i\psi_0(^3\Pi_{1y})dv=0,$$

and putting

$$D_{NQ}=Q_{NQ}{}^2,\quad Q_{NQ}=\int\psi^*(N)\Sigma x_i\psi_0(^1\Pi_x)dv$$
$$=\int\psi^*(N)\Sigma y_i\psi_0(^1\Pi_y)dv,\qquad(17)$$

we have

$$D_1=D_{NQ}/(1+z^2);\quad D_2=z^2D_{NQ}/(1+z^2).\qquad(18)$$

We then have

$$D_2/D_1=z^2=[R+(R^2+1)^{\frac{1}{2}}]^2.\qquad(19)$$

The validity of Eq. (19) may of course be impaired if case c influences become large.

As we go from Λ,S toward Ω,ω coupling, the wave function and energy of Q_0 (i.e., $^3\Pi_{0^+}$) remain in first approximation constant (see para-

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[8] Cf. R. S. Mulliken, J. Chem. Phys. **7**, 14 (1939), especially Eqs. (15), (3), (4). The quantity $G'D$ here is identical with $(P/e)^2$ of reference 2. It is preferable to calculate D values, rather than f values as in some of the writer's 1939 papers.

[*] The Q here has of course no connection with the symbol Q used for the Q complex of Q states.

graph following Eq. (4)), so that the intensity of $N \rightarrow Q_0$ should remain zero, as it is in Λ,S coupling. But case *c* tendencies and other secondary effects cause admixtures of wave functions of higher energy singlet (and triplet) states to enter the Q_0 wave function, and of triplet (and singlet) states to enter the N wave function. With the help of these, as further discussed in Section III, $N \rightarrow Q_0$ becomes allowed.

III. THEORY INCLUDING PERSISTENCE OF ATOMIC *J* QUANTIZATION

The effects of partial Ω,ω coupling in diatomic molecules are similar to those of partial J,j coupling in atoms. The main effect is usually an interaction between certain states of different spin but otherwise alike and belonging to the same electron configuration (*intra-configuration interactions*). Thus for the halogen Q_u states, interaction occurs between the $^3Q_1$ and the ^1Q as discussed in Section II.

Besides intra-configuration interactions, however, Ω,ω coupling, like J,j coupling in atoms, leads also to *inter-configuration interactions*. Generally, as with atoms, these are of secondary importance. Inter-configuration interactions are possible between any two states having the same parity (g or u) and the same Ω; if $\Omega=0$, the interacting states must be alike in the + or − property indicated in the symbols 0^+, 0^-.

Under some circumstances, inter-configuration may become comparable in magnitude to intra-configuration interactions. In familiar molecules, the most important inter-configuration interactions come, directly or indirectly, from "separate-atom-case-*c*" effects.* These effects occur when a set of molecular states belonging for Λ,S coupling to several distinct *molecular* electron configurations go over, on separation of the molecule into its two atoms, into states of a *single atomic* electron configuration.

For example, a large number of lower-energy states of any halogen molecule go over[2] on dissociation into states of the atomic configuration $p^5 \cdot p^5$. The latter, when the atoms are separate, gives states of three distinct energy values: $(^2P_{1\frac{1}{2}},{}^2P_{1\frac{1}{2}})$, $(^2P_{1\frac{1}{2}},{}^2P_{\frac{1}{2}})$, and $(^2P_{\frac{1}{2}},{}^2P_{\frac{1}{2}})$. If L and S in each atom are strongly coupled to form a J, there is a strong tendency for this coupling to persist even when the atoms combine to a molecule. That is, the type of coupling which occurs in the atoms, and which needs to be completely unscrambled if molecular wave functions corresponding to pure and definite molecular electron configurations are to be obtained, is partially retained in the molecule. Or conversely, starting from the molecular viewpoint, one may say that the tendency toward atomic-J quantization causes an interaction and partial scrambling of molecular states having different electron configurations.

Such interactions are called separate-atom-case-*c* effects of, say, *Type I*. Additional, less direct, separate-atom-case-*c* interactions (say, *Type II*) occur when molecular states derived from *one* atomic electron configuration interact with others derived from *another*. Interactions (often strong) between states with different electron configurations occur, of course, even for Λ,S coupling, in the case of states which are alike in parity, in S, in Λ, and, if $\Lambda=0$, in + or − sign in Σ^+ or Σ^-. These of course are not themselves case *c* effects. But such interactions *combined* with case *c* scrambling of states differing in Λ and S, but alike in Ω, give rise to Type II case *c* interactions. *Both* types of case *c* interactions must be considered in order to obtain an adequate explanation of the halogen $N \rightarrow Q$ spectra.

In discussing separate-atom-case-*c* interaction, it is best to think in terms of AO approximation wave functions. We are of course particularly interested in the N and Q halogen states. In AO approximation, these and various other states,[2] listed in Table I, are all derived from the union of two normal neutral halogen atoms each in a p^5, ^2P state. As a result of Type I case *c* interactions, all states of like case *c* classification in Table I interact more or less. For example, the wave function of state N, which if pure would be $\sigma\pi^4 \cdot \sigma\pi^4$, $^1\Sigma^+_g$ only, becomes polluted with a certain amount of the wave functions of $\sigma\pi^4 \cdot \sigma^2\pi^3$, $^3\Pi_{0^+g}$ and of a $^3\Sigma^-_g$ and a second $^1\Sigma^+_g$ state. All such Type I case *c* mixings for the N and Q states are listed in Table I.

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* One might also discuss united-atom-case-*c* effects, but this is not worth while here, since the united-atom approximation is of little significance for molecules such as the halogens.

It will be noticed that the $^3Q_1$ and ^1Q states are listed in Table I as perturbing each other; this is of course nothing else than the primary effect of partial Ω,ω coupling discussed in Section II. In addition, both states are perturbed (partial case c coupling) by three others in Table I. Since the states causing the Type I case c perturbation of N and Q lie well above N and probably[2] all definitely above Q, they should cause some lowering of the energy of N and especially of the Q states. Exceptional, however, is Q_0, for which there are no perturbing states in Table I. Hence we expect Type I case c influences to cause a *relative lowering of the energies of all the other Q states* as compared with Q_0. In particular, Q_{0^-} is pushed below Q_0; that is, the Q state $^3\Pi_0$, which for Λ,S coupling would have twofold degeneracy like the Q states $^1\Pi$, $^3\Pi_1$, and $^3\Pi_2$, must be split into two distinct components Q_{0^-} and Q_0, as was shown by Van Vleck.[9]

Equations whereby the magnitudes of the foregoing Type I case c energy effects can be estimated, provided we know the positions of the perturbing excited levels, have been given by Van Vleck for the states belonging to the 0^+_g and 0^-_u case c types.[10] A similar equation is obtained here for the 1_u case c type, to which $^3Q_1$ and ^1Q belong.

In order to obtain the desired equation for the 1_u type, one writes

$$\psi_i = a_{1i}\psi_0(^3\Pi_1) + a_{2i}\psi_0(^1\Pi) + a_{3i}\psi_0(^3\Delta_{1u}) + a_{4i}\psi_0(^3\Sigma_u^+)_1 + a_{5i}\psi_0(^3\Sigma_u^+)_1', \tag{20}$$

$i = 1\cdots 5$, where the various ψ_0's correspond to electron configurations as given in Table I. $\psi_0(^3\Sigma_u^+)_1$ and $\psi_0(^3\Sigma_u^+)_1'$ represent the $\Omega=1$ wave functions of two $^3\Sigma^+$ states. The order in which the functions are written in Eq. (20) is supposed to be that of increasing energy. The process of determining the coefficients in Eq. (20) leads in the usual way to a secular equation which is found to be as follows:*

$$\begin{vmatrix} E_0-\frac{1}{2}X-E & -\frac{1}{2}a\Omega & -2^{-\frac{1}{2}}a & -\frac{1}{2}a & -2^{-\frac{1}{2}}a \\ -\frac{1}{2}a\Omega & E_0+\frac{1}{2}X-E & 2^{-\frac{1}{2}}a & -\frac{1}{2}a & 2^{-\frac{1}{2}}a \\ -2^{-\frac{1}{2}}a & 2^{-\frac{1}{2}}a & H_{33}-E & 0 & 0 \\ -\frac{1}{2}a & -\frac{1}{2}a & 0 & H_{44}-E & \epsilon \\ -2^{-\frac{1}{2}}a & 2^{-\frac{1}{2}}a & 0 & \epsilon & H_{55}-E \end{vmatrix} = 0 \tag{21}$$

In Eq. (21), E_0, X, and a are as defined in Section II. Eq. (21) applies to the case of the AO electron configuration $\sigma\pi^4\cdot\sigma^2\pi^3$ (briefly, $\pi^3\sigma$); it applies also to the two-electron configuration $\pi\cdot\sigma$, provided the sign before every a is reversed.* Eq. (21) really covers two cases, $\Omega=+1$ and $\Omega=-1$; the sign of Ω affects, however, only the sign of the matrix element H_{12} and H_{21}.

In the case that $a/(H_{33}-E_0)$, $a/(H_{44}-E_0)$, and $a/(H_{55}-E_0)$ are small compared with X, the $^3\Pi_1$ and $^1\Pi$ states interact mainly with each other, and, approximately, Eq. (21) factors, giving Eq. (6) for these two states as in Section II.

Equation (21) may be rewritten in a form more convenient for our purposes if in Eq. (20)

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[9] J. H. Van Vleck, Phys. Rev. **40**, 544 (1932).

[10] Reference 9, pp. 564–8.

* The problem is essentially the same as that of the 1_u states obtained by bringing together two $p\,^2P$ atoms (cf. reference 9 for the corresponding problem for the 0^+ and 0^- states). For two $p\,^2P$ atoms, the wave functions of Eq. (20), for $\Omega=+1$, take forms as follows:

$$\psi_0(^3\Pi_1,{}^1\Pi) = 2^{-\frac{1}{2}}[\pi_+(1)\sigma'(2)-\pi_+'(1)\sigma'(2) \mp\sigma'(1)\pi_+(2)\pm\sigma(1)\pi_+'(2)][\alpha(1)\beta(2)\pm\alpha(2)\beta(1)].$$

The upper signs refer to $^3\Pi_1$, the lower to $^1\Pi$; π_+ means an $np\pi$ AO with positive angular momentum; the primed and unprimed symbols refer to the two atoms; α and β are the spin wave functions.

$$\psi_0(^3\Delta_{1u}) = 2^{-\frac{1}{2}}[\pi_+(1)\pi_-'(2)-\pi_+'(1)\pi_+(2)]\beta(1)\beta(2)$$

$$\psi_0(^3\Sigma_u^+)_1 = \tfrac{1}{2}[\pi_+(1)\pi_-'(2)-\pi_-'(1)\pi_+(2) -\pi_+'(1)\pi_-(2)+\pi_-(1)\pi_+'(2)]\alpha(1)\alpha(2)$$

$$\psi_0(^3\Sigma_u^+)_1' = 2^{-\frac{1}{2}}[\sigma(1)\sigma'(2)-\sigma'(1)\sigma(2)]\alpha(1)\alpha(2).$$

Using these wave functions, one sets up

$$H_{ij} = \int\psi_i^*(\Sigma a_i\mathbf{l}_i\cdot\mathbf{s}_i)\psi_j d\tau,$$

—cf. Eqs. (2), —with the spin-orbit energy set up in proper operator form. The integrals can be worked out in terms of simple matrix elements of the components of $\mathbf{l}_i$ and $\mathbf{s}_i$.[6] In this way we obtain essentially the nondiagonal matrix elements in Eq. (21), except for the electrostatic element ϵ which corresponds to a non-case-c interaction. It is not difficult to show that the matrix elements for the case c interaction of the 1_u states of two p^5, ^2P atoms are the same as those for two p, ^2P atoms, except that every a is replaced by $-a$: in Eq. (21) in the text, this replacement has already been made.

TABLE I. *Type I case c pollutions of N and Q states. This table is based on Table III of reference 2. There are several additional states derived from configurationally unexcited atoms, but which do not interact with the N and Q states.*

State				
NAME	CASE *c* TYPE	Λ,S TYPE	AO ELEC. CONFIGN.	Λ,S TYPE AND AO ELECTRON CONFIGNS. OF POLLUTING STATES
N	0_g^+	$^1\Sigma_g^+$	$\pi^4\sigma\cdot\sigma\pi^4$	$\pi^4\sigma\cdot\sigma^2\pi^3$, $^3\Pi_{0^+g}$; $\pi^3\sigma^2\cdot\sigma^2\pi^3$, $^3\Sigma_g^-$ and $^1\Sigma_g^+$
$^3Q_2$	2_u	$^3\Pi_{2u}$	$\pi^4\sigma\cdot\sigma^2\pi^3$	$\pi^3\sigma^2\cdot\sigma^2\pi^3$, $^3\Delta_{2u}$
$^3Q_1$	1_u	$^3\Pi_{1u}$	$\pi^4\sigma\cdot\sigma^2\pi^3$	^1Q; $\pi^3\sigma^2\cdot\sigma^2\pi^3$, $^3\Delta_{1u}$ and $^3\Sigma_u^+$; $\pi^4\sigma\cdot\sigma\pi^4$, $^3\Sigma_u^+$
Q_{0^-}	0_u^-	$^3\Pi_{0^-u}$	$\pi^4\sigma\cdot\sigma^2\pi^3$	$\pi^3\sigma^2\cdot\sigma^2\pi^3$, $^1\Sigma_u^-$ and $^3\Sigma_u^+$; $\pi^4\sigma\cdot\sigma\pi^4$, $^3\Sigma_u^+$
Q_0	0_u^+	$^3\Pi_{0^+u}$	$\pi^4\sigma\cdot\sigma^2\pi^3$	none
^1Q	1_u	$^1\Pi_u$	$\pi^4\sigma\cdot\sigma^2\pi^3$	$^3Q_1$; $\pi^3\sigma^2\cdot\sigma^2\pi^3$, $^3\Delta_{1u}$ and $^3\Sigma_u^+$; $\pi^4\sigma\cdot\sigma\pi^4$, $^3\Sigma_u^+$.

we start with $\psi(^3Q_1)$ and $\psi(^1Q)$, as given by Eqs. (5) and (12), instead of with $\psi_0(^3\Pi_1)$ and $\psi_0(^1\Pi)$.

We then (cf. Eq. (7) for H_{11} and H_{22} here) obtain:

$$\begin{vmatrix} E_0-\tfrac{1}{2}(X^2+a^2)^{\frac{1}{2}}-E & 0 & -2^{-\frac{1}{2}}\rho a & -\tfrac{1}{2}\sigma a & -2^{-\frac{1}{2}}\rho a \\ 0 & E_0+\tfrac{1}{2}(X^2+a^2)^{\frac{1}{2}}-E & -2^{-\frac{1}{2}}\sigma a & \tfrac{1}{2}\rho a & -2^{-\frac{1}{2}}\sigma a \\ -2^{-\frac{1}{2}}\rho a & -2^{-\frac{1}{2}}\sigma a & H_{33}-E & 0 & 0 \\ -\tfrac{1}{2}\sigma a & \tfrac{1}{2}\rho a & 0 & H_{44}-E & \epsilon \\ -2^{-\frac{1}{2}}\rho a & -2^{-\frac{1}{2}}\sigma a & 0 & \epsilon & H_{55}-E \end{vmatrix} = 0 \tag{22}$$

In Eq. (22),

$$\rho=(z-1)/(1+z^2)^{\frac{1}{2}}, \quad \sigma=(z+1)/(1+z^2)^{\frac{1}{2}}, \tag{23}$$

with $z=R+(R^2+1)^{\frac{1}{2}}$, $R=X/a$ (cf. Eq. (13)). [Eq. (22) applies for the configuration $\sigma\pi^4\cdot\sigma^2\pi^3$; for the configuration $\pi\cdot\sigma$, σ and ρ replace each other throughout and, in addition, the sign before each a in the first row and in the first column is reversed.]

In the case that ϵ, $a/(H_{33}-H_{kk})$, $a/(H_{44}-H_{kk})$, and $a/(H_{55}-H_{kk})$, where $H_{kk}=H_{11}$ or H_{22}, are not too large, the two lower roots of Eq. (22) can be obtained approximately as follows, by expanding Eq. (22) and keeping the main terms:

$$\begin{aligned} E(^3Q_1)=H_{11}&-\tfrac{1}{2}\rho^2a^2/(H_{33}-H_{11}) \\ &-\tfrac{1}{4}\sigma^2a^2/(H_{44}-H_{11}) \\ &-\tfrac{1}{2}\rho^2a^2/(H_{55}-H_{11}), \end{aligned} \tag{24}$$

$$\begin{aligned} E(^1Q)=H_{22}&-\tfrac{1}{2}\sigma^2a^2/(H_{33}-H_{22}) \\ &-\tfrac{1}{4}\rho^2a^2/(H_{44}-H_{22}) \\ &-\tfrac{1}{2}\sigma^2a^2/(H_{55}-H_{22}). \end{aligned} \tag{25}$$

Eqs. (24), (25) correspond to the ordinary second-order perturbation energy expressions for the perturbation of $^3Q_1$ and ^1Q by the other three states. H_{11} and H_{22} are the energies $E_0\pm\frac{1}{2}(X^2+a^2)^{\frac{1}{2}}$ of $^3Q_1$ and ^1Q, as given by Eq. (7) after allowing for their mutual interaction.

While considering Type I case *c* interactions, it will be useful to give equations analogous to Eqs. (24) and (25) but applicable to the states $N\,^1\Sigma_g^+$ and $Q_{0^-}\,^3\Pi_{0^-u}$. The former state corresponds to the lowest energy root of a secular equation for the 0_g^+ states of Table I, the latter to the lowest root of a secular equation for the 0_u^- states. These complete secular equations have been given by Van Vleck,† and it is only necessary to expand them under similar assumptions to those made above in obtaining Eqs. (24) and (25) from Eq. (23).

The equation for state N is:

$$E_N=H_{11}-a^2/(H_{22}-H_{11})-\epsilon^2/(H_{33}-H_{11}), \tag{26}$$

where H_{11}, H_{22}, H_{33} are the unperturbed AO approximation energies of N $\sigma\pi^4\cdot\sigma\pi^4$, $^1\Sigma^+{}_g$, of $\sigma^2\pi^3\cdot\sigma\pi^4$, $^3\Pi_{0^+g}$, and of $\sigma^2\pi^3\cdot\sigma^2\pi^3$, $^1\Sigma^+{}_g$; $\epsilon=H_{13}$ represents an electrostatic matrix element, occurring even for Λ,S coupling.

The equation for the Q_{0^-} state is:

$$\begin{aligned} E(^3\Pi_{0^-u})=H_{11}&-\tfrac{1}{2}a^2/(H_{22}-H_{11}) \\ &-\tfrac{1}{2}a^2/(H_{44}-H_{11})-a^2/(H_{55}-H_{11}), \end{aligned} \tag{27}$$

where H_{11} refers to $\sigma^2\pi^3\cdot\sigma\pi^4$, $^3\Pi_{0^-u}(Q_{0^-})$, H_{22} to $\sigma^2\pi^3\cdot\sigma^2\pi^3$, $^1\Sigma^-{}_u$, H_{44} and H_{55} to $\sigma^2\pi^3\cdot\sigma^2\pi^3$, $^3\Sigma^+{}_u$

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† Both secular equations are of the form given by Eq. (16) of reference 9, with the sign before each a reversed to correspond to the union of two atoms each of configuration p^5, instead of two atoms each with one p electron.

and $\sigma\pi^4\cdot\sigma\pi^4$, ${}^3\Sigma^+{}_u$ (H_{44} and H_{55} here are the same as in Eqs. (24), (25)).

Equations (24)–(27) include, of course, only Type I case *c* effects and do not include the perturbing effects of various higher excited states. Especially important among the latter should be strong perturbations by certain ionic states, namely for state *N* by the $\sigma^2\pi^4\cdot\pi^4$, ${}^1\Sigma_g{}^+$ ionic state and for the *Q* states by the $\sigma^2\pi^4\cdot\sigma\pi^3$, ${}^3\Pi_u$ and ${}^1\Pi_u$ ionic states (the configurations given are of course AO ones). Admixture of the wave functions of these ionic states into the ordinary AO functions of states *N* and *Q* carry the latter over toward the MO approximation wave functions.

Type II case *c* effects should come in mainly as an indirect result of these ionic admixtures. For example, because of case *c* influences (cf. Section VI), $\sigma^2\pi^4\cdot\sigma\pi^3$, ${}^3\Pi_{0^+u}$ must be more or less mixed with the following three other states having the same case *c* classification $0^+{}_u$ and the same atomic electron configuration $p^6\cdot p^4$: $\sigma^2\pi^4\cdot\pi^4$, ${}^1\Sigma_u{}^+$, $\sigma^2\pi^4\cdot\sigma^2\pi^2$, ${}^1\Sigma_u{}^+$ and ${}^3\Sigma_u{}^-$. Strong perturbation of Q_0 (i.e., $\sigma^2\pi^3\cdot\sigma\pi^4$, ${}^3\Pi_{0^+u}$) by the ionic $\sigma^2\pi^4\cdot\sigma\pi^3$, ${}^3\Pi_{0^+u}$, the latter admixed with a considerable amount of V $\sigma^2\pi^4\cdot\pi^4$, ${}^1\Sigma_u{}^+$, doubtless represents the (Type II case *c*) mechanism whereby Q_0 acquires that admixture of *V* wave function which has been suggested[2, 9] as a likely cause of the occurrence and anomalously high intensity of $N\rightarrow Q_0$ in the heavier halogens. Admixture of *V* in Q_0 should cause considerable intensity in $N\rightarrow Q_0$ in view of the fact that calculations show that $N\rightarrow V$ should have extraordinarily high intensity.[11] The intensity of $N\rightarrow Q_0$ will be further discussed in Section VI.

The various above-discussed perturbations of the AO-approximation *N* and *Q* wave functions should depress these states (that is, lower their energies) considerably. The depressions produced in the various individual states of the *Q* complex by the ionic ${}^3\Pi_u$, ${}^1\Pi_u$ and other high excited states, though fairly large, should presumably all be nearly equal.

This is not true, however, of the Type I case *c* depressions. On putting in numerical values for the estimated energy intervals (see below) and for *a* in Eqs. (24), (25), (27), one finds that the ${}^3Q_1$ and especially the ${}^1Q$ and the $Q_{0^-}({}^3\Pi_{0^-u})$ levels for Br_2 and especially I_2 should be depressed very noticeably by Type I case *c* effects. But since no such effects act on Q_0, the other members of the *Q* complex should, as already noted, all be depressed relatively to the latter. Thus the ${}^3\Pi_0$ level should be split into Q_0 (upper component) and Q_{0^-} (lower component), and the intervals between Q_0 and the ${}^3Q_1$ and ${}^1Q$ levels should be altered as compared with Eqs. (11) of Section II. In Sections IV and V, we shall examine experimental evidence for Br_2 and I_2 bearing on these questions.

The argument of the preceding paragraph is based on the assumption that all the denominators in Eqs. (24), (25), (27) are positive. Estimates of the values of these can be found for I_2 in Table III of reference 1. According to this table, whose energy estimates are based on the MO approximation, these denominators are indeed positive, and not too small to make Eqs. (24)–(27) represent tolerably good approximations for the Type I case *c* energy effects.*

In an earlier paragraph, a Type II case *c* mechanism which may account for the high intensity of $N\rightarrow Q_0$ (which would be forbidden in the approximation of Section II) has been mentioned. A second possible case *c* mechanism, this time of Type I, has also been proposed.[12] The latter involves perturbation of $N\rightarrow{}^1\Sigma_g{}^+$ by Q_{0g} ($\sigma^2\pi^3\cdot\sigma\pi^4$, ${}^3\Pi_{0^+g}$). If the *N* wave function contains admixture of Q_{0g}, it becomes able to combine with Q_0, since ${}^3\Pi_{0^+g}\rightarrow{}^3\Pi_{0^+u}$ is allowed.

For any second-order energy perturbation equation there is a corresponding first-order wave function equation; thus corresponding to

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[11] R. S. Mulliken, J. Chem. Phys. 7, 20 (1939).

* The only possible question is in regard to $(H_{33}-H_{22})$ and $(H_{44}-H_{22})$ of Eq. (25), and $(H_{22}-H_{11})$ and $(H_{44}-H_{11})$ of Eq. (27), for all of which the upper state (${}^1\Sigma_u{}^-$, ${}^3\Delta_{1u}$, or ${}^3\Sigma_u{}^+$) belongs to the AO electron configuration $\sigma^2\pi^3\cdot\sigma^2\pi^3$. AO approximation calculations indicate that these states should lie only a little above the *Q* states, perhaps near the $Q_g(\sigma^2\pi^3\cdot\sigma\pi^4$, ${}^3\Pi_g$, ${}^1\Pi_g)$ states. Perturbations by higher energy states should, however, increase the separations (by depressing the *Q* states much more than the $\sigma^2\pi^3\cdot\sigma^2\pi^3$ ${}^1\Sigma_u{}^-$, ${}^3\Delta_u$, and ${}^3\Sigma_u{}^+$ states), tending to make them accord with the MO approximation predictions. On the whole, it seems fairly certain that the denominators just discussed are all positive, and likely that they are not excessively small. It is *possible*, however, that some of them may be rather small; in this event, Eq. (21) and Van Vleck's secular equations should be used instead of Eqs. (25) and (27) if more than rough qualitative conclusions are desired.

[12] Reference 2, pp. 564 and 314.

TABLE II. *Interpretation of data on the N→Q complex.*

Molecule	Peak	Data[1,2]		Interpretation I[3]			Interpretation II[3]		
		ν_{max}	$\Sigma G'D\times10^4(A^2)$	Q level	ν_{max}	$D\times10^4(A^2)$	Q level	ν_{max}	$D\times10^4(A^2)$
F_2	*A*	34500	6.8*	$^1\Pi$	34500	3.4			
Cl_2	*B*	23550	1.1	$^3\Pi_1$	[23240]	[0.05]			
				$^3\Pi_{0+}$	23550	1.0			
	A	30300	56	$^1\Pi$	30300	28			
Br_2				$^3\Pi_1$	[18630]	[3.0]	$^3\Pi_1$	20730	20
	B	20730	46	$^3\Pi_{0+}$	20730	40	$^3\Pi_{0+}$	[22800]	20
	A	24300	114	$^1\Pi$	24300	57	$^1\Pi$	24300	50
I_2	*B*	13660	(3)	$^3\Pi_1$	13660	(2)	$^3\Pi_1$	13660	(2)
	A	19200	620*	$^3\Pi_{0+}$	19200	610	$^3\Pi_{0+}$	19200	610
				$^1\Pi$	[19820]	[6]	$^1\Pi$	[18920]	[3]

[1] For further details, and data on ICl, IBr, BrCl, cf. reference 1, p. 562, and J. L. Binder, Phys. Rev. **54**, 114 (1938).

[2] The $\Sigma G'D$ values (cf. Eq. (15)) and ν_{max} values are based on sources given in reference 1, p. 562, also reference 3 (Cl_2), reference 13 (Br_2), and reference 16 (I_2). The $\Sigma G'D$ values have been evaluated from Eq. (15), except those marked by asterisks which have been evaluated only rather roughly. The $G'D$ value for peak *B* of I_2 is an exceedingly rough and uncertain estimate based on appearance pressure data of Professor W. G. Brown (cf. Phys. Rev. **38**, 1187 (1931)). The quantity $G'D$ here is identical with the quantity $(P/e)^2$ of reference 1. The unit used for *D* is the square angstrom (A^2).

[3] See text for explanation of the two interpretations. Quantities in brackets are *calculated* values (see Table III).

Eq. (26) we have

$$\psi(N)\approx\psi_0(N)-[a/(H_{22}-H_{11})]\psi_0(Q_{0g})$$
$$-[\epsilon/(H_{33}-H_{11})]\psi_0(\sigma^2\pi^3\cdot\sigma^2\pi^3,\ ^1\Sigma_g{}^+). \quad (28)$$

For iodine, $a=5067$ cm^{-1} (cf. Table III), while $H_{22}-H_{11}$ can be estimated as not far from 25,000 cm^{-1}. This would mean that $\psi_0(Q_{0g})$ would appear in Eq. (28) with a coefficient about 0.2 as large as that of $\psi_0(N)$. [The corresponding energy depression, from Eq. (26), would be about 1000 cm^{-1}.] Because of the presence of $\psi_0(Q_{0g})$ admixture in $\psi_0(N)$, $N\rightarrow Q_0$ should now occur with a dipole strength $(0.2)^2$, i.e., 0.04, as large as that for pure $Q_{0g}\rightarrow$ pure Q_{0u},—or somewhat less, say 0.03 instead of 0.04, because of the rather strong ionic admixtures in $\psi(N)$ and $\psi(Q_0)$. Whether perturbation of *N* by Q_{0g} can explain the observed intensity of $N\rightarrow Q_0$ depends, then, on how strong pure $Q_{0g}\rightarrow$pure Q_{0u} would be. We shall leave this matter open until the further discussion of $N\rightarrow Q_0$ transitions in Section VI.

IV. Analysis of Experimental Data for F_2, Cl_2 and Br_2

With the aid of the theoretical relations of Sections II and III, and of recent new experimental data, conclusions previously given by the writer[2,3] and modified by Bayliss and his collaborators[4] are here systematically reviewed. The most likely revised interpretations of the available evidence are summarized in Tables II and III. The analysis generally confirms but clarifies the earlier interpretations, and yields some interesting new points.

Some general remarks must first be made about the quantity $\Sigma G'D$ in the fourth column of Table II.[8] In general, (cf. Eq. (15)), the quantity $3.83\times10^{-3}\int k\nu d\nu/\nu$ is conveniently taken as an experimental measure of absorption strength. This should be equal to $G'D$ if the absorption region in question belongs to a single transition, but if it results from an overlapping of regions belonging to two or more transitions, it should be equal to a sum $\Sigma G'D$ taken over these transitions. Since $G'=2$ for $N\rightarrow {}^3Q_1$ and for $N\rightarrow {}^1Q$, but $G'=1$ for $N\rightarrow Q_0$, we cannot evaluate experimental *D*'s until we have identified the absorption region and know its G', in case it is simple, or until we have analyzed it if it is complex. With this in mind, we can proceed to the discussion of specific spectra.

Let us begin with Cl_2 and Br_2. Bayliss and collaborators[4] have shown that the $N\rightarrow Q$ absorption continuum of each of these molecules is a superposition of two continua *A* and *B*. In Cl_2, peak *B* is about 1/66 as strong as peak *A*, and the two peaks are 6750 cm^{-1} apart; in Br_2 peak *B* is about a third as strong as *A* and 3570 cm^{-1} from *A*. In both cases, *B* really appears in the spectrum not as a peak but as a shoulder on the side of the main peak *A*.

In Cl_2 the *A*,*B* interval is so large, according to Aickin and Bayliss,[4] and the spin-orbit coup-

TABLE III. *Interpretation of data on the Q complex.*

MOLECULE	COUPLING COEFFICIENTS[1,2]			RELATIVE ENERGIES (CM^{-1})							DIPOLE STRENGTH RATIO D_2/D_1	
				CALCULATED[3]				OBSERVED[4]				
	a	X	R (IF $\lambda=1$)	$^3\Pi_2$	$^3\Pi_1$	$^3\Pi_0$	$^1\Pi$	$^3\Pi_{0^+}-{}^3\Pi_1$	$^1\Pi-{}^3\Pi_{0^+}$	$^1\Pi-{}^3\Pi_1$	CALC.[3]	OBS.[4]
Cl_2	587	7040	12.0	−281	0	306	7060	—	6750	—	590	>50
Br_2	2457	I: 5110	2.09	−947	0	1510	5670	2100±	3570	—	19	—
		II: 2600	1.06	−742	0	1715	3570	2100±	—	3570	6.3	2.5
I_2	5067	I: [3500]	[0.69]	−1207	0	3860	6160	5540	—	—	3.8	—
		II: [1000]	[0.2]	− 407	0	4660	5260	5540	—	—	1.5	—

[1] The coupling coefficients a correspond to normal neutral atoms (cf. reference 2).

[2] The two sets of X and R values for Br_2 and I_2 correspond to the two interpretations I and II of Table II. The values for I_2, in brackets, are estimated by extrapolation from Cl_2 and Br_2.

[3] The calculated quantities are based on a and X of the preceding columns.

[4] The "observed" quantities are from the following sources: Cl_2, reference 4; Br_2, reference 13 for $^1\Pi-{}^3\Pi$ and reference 14 for $^3\Pi_{0^+}-{}^3\Pi_1$; I_2 reference 16. The $^3\Pi_{0^+}-{}^3\Pi_1$ intervals are based on the minima of the corresponding potential energy curves, except that for I_2 the interval is based on continua maxima (the interval from potential minima, 5510±400 cm^{-1}—see reference 1—is, however, nearly the same). The $^1\Pi-{}^3\Pi_{0^+}$ or $^1\Pi-{}^3\Pi_1$ intervals are based on continua maxima.

ling coefficient a is so small,[2] that the coupling must be close to the Λ,S type. Peak A must then be exclusively $N\rightarrow{}^1Q$, while peak B must be either $N\rightarrow{}^3Q_1$ or $N\rightarrow Q_0$ or both.[4] In either case, the frequency interval between peaks must approximately equal the Λ,S singlet-triplet interval X. Knowing X and a and setting $\mu=1$ as an approximation in Eq. (9), we can then calculate theoretically the intensity ratio D_2/D_1 of $N\rightarrow{}^1Q$ to $N\rightarrow{}^3Q_1$ by Eq. (19). The result is $D_2/D_1=590$. From this and the observed $G'D$ value[4] of 56×10^{-4} (in A^2) for peak A we calculate that $G'D$ should be 0.095×10^{-4} for $N\rightarrow{}^3Q_1$. Since the observed $\Sigma G'D$ for peak B (see Table II, footnote 2), is about 1.1×10^{-4}, it becomes probable that peak B is mainly $N\rightarrow Q_0$. The interpretation given in Tables II and III has been worked out on this basis.

That peak B is mainly $N\rightarrow Q_0$ is also in harmony with the fact that the observed weak discrete absorption bands of Cl_2 belong to $N\rightarrow Q_0$. If $N\rightarrow{}^3Q_1$ were comparable to $N\rightarrow Q_0$ in intensity, some of its bands would probably have been observed.

It is clear that the one observed continuum peak for F_2 must be $N\rightarrow{}^1\Pi$, since a is smaller and R probably larger for F_2 than for Cl_2. The B peak of F_2 must be very weak, since neither it nor possible accompanying bands have been observed.

In seeking to interpret the A and B peaks of bromine vapor,[13] we first note that the interval between the *minima* of the Q_0 and $^3Q_1$ potential energy curves, as determined by Darbyshire,[14] is probably not far from 2100 cm^{-1}. Since about the same separation (or if anything a somewhat smaller separation, see below) should exist between the corresponding continua maxima, the possibility that the A,B separation of 3570 cm^{-1} could be $Q_0-{}^3Q_1$ seems to be ruled out. Franck-Condon evidence supports this conclusion.[4,13,14]

There remain two possibilities: the 3570 cm^{-1} A,B separation may be either $^1Q-Q_0$ or $^1Q-{}^3Q_1$. The first alternative implies that the $N\rightarrow{}^3Q_1$ peak must be weak and fall on the long wavelength side of B, the second that the $N\rightarrow Q_0$ peak must be rather weak and form a part of the A or B peak. As we shall see in the following paragraphs, either alternative seems to be compatible with existing information. The evidence on the whole favors the first interpretation (interpretation I of the tables), but unfortunately none of it seems quite decisive.

Let us begin with the second interpretation (interpretation II of the Tables). If peak A is $N\rightarrow{}^1Q$ and B is $N\rightarrow{}^3Q_1$ and if we can neglect case c effects, we can calculate the quantity R by means of Eq. (11), assuming $\mu=1$, also (since a is known), the quantity X by Eq. (9): see Table III. Knowing R, the dipole strength ratio D_2/D_1 for the two peaks can be calculated. The resulting value of 6.3 (cf. Table III) perhaps does not disagree too badly with the observed value of 2.5, considering uncertainties as to $\mu,a,$

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[13] A. P. Acton, R. G. Aickin and N. S. Bayliss, J. Chem. Phys. **4**, 474 (1936); N. S. Bayliss, Proc. Roy. Soc. **A158**, 551 (1937).

[14] O. Darbyshire, Proc. Roy. Soc. **A159**, 93 (1937).

the distance $B-A$, and the influence of case c tendencies. Still, it does not give very strong support to interpretation II.

The energy interval $Q_0-{}^3Q_1$ can also be calculated (cf. Table III). The calculated value of 1715 cm^{-1} is in reasonable agreement with the 2104 cm^{-1} interval observed for the potential minima, when allowance is made for case c influences, which tend to lower the energy of ${}^3Q_1$ (cf. Section III). A similar but considerably larger effect of the same kind is present in iodine (see below).

According to the preceding calculation, the $N\rightarrow Q_0$ peak should lie about midway between A and B peaks. In earlier discussions, it has generally been supposed to form part of the A or of the B peak.[2–4] Examination of the curve of absorption coefficient against frequency as given by Bayliss[13] indicates that this could be the resultant of three superposed curves B, C, and A with the C peak about midway between the other two. A plausible redistribution of the A and B intensities among A, B, and C is given in interpretation II of Table II. According to this, C is weaker (in $G'D$ strength) than either A or B, but still of considerable intensity. The latter seems necessary in view of the relative conspicuousness of the $N\rightarrow Q_0$ discrete bands in the Br$_2$ absorption spectrum.

Now let us consider interpretation I:

$$(A=N\rightarrow{}^1\Pi,\ B=N\rightarrow{}^3\Pi_{0^+}).$$

According to this, a weak $N\rightarrow{}^3\Pi_1$ or C peak should lie at about 2100 cm^{-1} lower frequency than B, 2100 cm^{-1} being the known $Q_0-{}^3Q_1$ interval as obtained from the potential minima. This gives the ${}^1Q-{}^3Q_1$ interval to be about 5670 cm^{-1}. Proceeding as we did above for interpretation II, we obtain $X=5110$ cm^{-1}, $R=2.09$, and $D_2/D_1=19$ (cf. Table III). From $G'D=114\times10^{-4}\text{A}^2$ for $N\rightarrow{}^1Q$, we then calculate $G'D=6.0\times10^{-4}$ for $N\rightarrow{}^3Q_1$. On examination of the intensity curve of the B continuum as given by Bayliss,[13] it seems possible that a small C peak of this magnitude could be hidden in the low frequency tail of B, a region where discrete $N\rightarrow Q_0$ bands also occur.* Thus either of the interpretations I and II seems compatible with the observed shape of the B continuum, so far as can be seen from inspection of Bayliss' curve.[13]

A possible argument in favor of interpretation I is the reported relative weakness of the discrete bands of $N\rightarrow{}^3Q_1$ as compared with those of $N\rightarrow Q_0$ (cf. reference 1, p. 562); but the observations are too qualitative to be conclusive.

The strongest argument in favor of interpretation I seems to be that the segment of potential energy curve obtained by Bayliss from the position and shape of the B peak fits very well as a continuation of the Morse curve of the Q_0 state, but is too high to be fitted, without forcing, onto that of the ${}^3Q_1$ state (see the curves in reference 4). In harmony with this, the $\nu_{\max}$ predicted by the Franck-Condon principle from the Q_0 Morse curve agrees closely with that of the B peak.[13] The argument is supported by the existence of a similar fit between Morse curve and $\nu_{\max}$ of $N\rightarrow Q_0$ in iodine (cf. Section V); in the latter case there is no doubt that $\nu_{\max}$ belongs to $N\rightarrow Q_0$. The argument is (on the whole) enhanced by the fact that in chlorine,[4] the accurate potential energy curve of Q_0 (constructed according to the Rydberg-Klein method) runs much *lower* than the Morse curve in that part of the curve which is responsible for $\nu_{\max}$. A careful construction of the lower parts of the Br$_2$ curves by the Rydberg-Klein method should have value in deciding between interpretations I and II.

Some uncertainty is introduced into the preceding arguments as a result of theoretical calculations reported in a separate paper.[1] According to these, the dipole strength D for the $N\rightarrow{}^{1,3}Q_1$ transitions diminishes rapidly with increasing internuclear distance r. For a given potential energy curve, this would cause an increase in $\nu_{\max}$ as compared with what one would predict from the usual tacit assumption that D varies only slightly with r. In the case of $N\rightarrow Q_0$ it has not been feasible to make calculations on D. It seems likely that here also D may vary rapidly with r, although it is not excluded that D_{NQ_0} may be near a maximum at normal internuclear separation. In any case, it appears that the deduction of segments of potential energy curves from intensity distributions in absorption continua may often need revision

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* A careful remeasurement of the absorption coefficient in this region, with a foreign gas added at high pressure to suppress the band structure, as in the work of Rabinowitch and Wood on iodine (cf. reference 16), might be valuable.

to allow for such effects. It appears further that caution is needed in interpreting observed intervals between the $\nu_{\max}$ of continua as equal to vertical intervals between corresponding potential energy curves.

A point worth mentioning is the possibility of predissociation in the $N\rightarrow Q_0$ bands as a result of the crossing of the Q_0 by ^1Q curve (cf., however, the discussion at the end of Section V). Bayliss and Rees[4] suggest that such crossing is the cause of possible vibrational perturbations reported by Darbyshire[14] in the neighborhood of the fourth vibrational level of Q_0. As Bayliss and Rees have shown, it is likely that the crossing of Q_0 by ^1Q is at about this height, on the outer limb of the Q_0 potential energy curve. The point of crossing, however, is not affected by the choice between interpretations I and II.[15]

It is difficult to understand that perturbations rather than predissociation should occur near the crossing point. However, no rotational analysis has been made of bands involving vibrational levels near the supposed location of the perturbations or predissociation.

V. Analysis of Experimental Data: Iodine

In the iodine vapor spectrum there is a very weak B peak at λ7320, which can be immediately identified as $N\rightarrow{}^3Q_1$, and a strong A peak near λ5200 (cf. Table I). Whereas in the other halogens only an unimportant fraction of the total absorption strength is in the bands, in iodine the A peak is actually within the banded part of the spectrum ($N\rightarrow Q_0$ bands); it is, however, not far from the convergence limit of the latter. As is well known, attempts to measure true absorption strengths in regions of discrete bands are fraught with dangers. This difficulty exists over the long wave-length half of the A region of iodine. Rabinowitch and Wood, however, have overcome it by blotting out the band structure with the use of a pressure of 500 mm of foreign gas.[16] The resulting curve of absorption coefficient against frequency is much smoother, and has its peak at a lower frequency, than those of earlier observers who used iodine vapor by itself.

Examination of these results of Rabinowitch and Wood shows conclusively that at least a considerable fraction if not most of the intensity of the A region belongs to $N\rightarrow Q_0$ (bands and continuum). It shows also that $N\rightarrow{}^1Q$, if present in the same region, must be much weaker than $N\rightarrow Q_0$, or else have its peak at nearly the same frequency, or both.* Hence, definitely, $\nu_{\max}$ of A is $\nu_{\max}$ of $N\rightarrow Q_0$, while the position of $\nu_{\max}$ of $N\rightarrow{}^1Q$ remains to be determined.

In an effort to do this, one can estimate values of X and R for I_2 by extrapolation from the values for Cl_2 and Br_2. Knowing a and R and the position of $\nu_{\max}$ of $N\rightarrow{}^3Q_1$, the position of $N\rightarrow{}^1Q$ (and of $N\rightarrow Q_0$) can be calculated. Two estimates for X and R, corresponding, respectively, to the two interpretations of the Br_2 continuum, are given in Table III. Let us call these interpretations I and II for I_2. Interpretation I locates $N\rightarrow{}^1Q$ at 600 cm^{-1} higher frequency, and interpretation II at 600 cm^{-1} lower frequency, than the peak of the A region. The *intensity* of $N\rightarrow{}^1Q$, obtained from D_2/D_1 calculated in the usual way, combined with the (unfortunately very uncertain**) D value of $N\rightarrow{}^3Q_1$, comes out a very small fraction of the observed $\Sigma G'D$ value of the A region in either case (cf. Table II). From this, in harmony with the experimental evidence noted above, there seems to be little doubt that the $N\rightarrow{}^1Q$ continuum must be a weak one buried under the much stronger continuum and bands of the $N\rightarrow Q_0$ transition. No reasonable variation in the estimated X value for I_2 could change this conclusion, as can be seen from Table III**.

It will be noted that the observed interval $Q_0-{}^3Q_1$ (5540 cm^{-1} from the interval between the A and B peaks, confirmed by the value

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[15] Bayliss and Rees' assumption (see their figure) that the Q_0 curve crosses the Q_1 curve a second time at an internuclear distance corresponding to the normal state of the molecule is in disagreement with both interpretations I and II, and seems very improbable theoretically.

[16] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. 32, 540 (1936).

* A shoulder normally present on the low frequency side of the A region of iodine nearly disappears when foreign gas pressure is high enough, and it may be supposed that it would disappear entirely in the limit. At any rate, its location does not at all conform to that expected for $N\rightarrow{}^1Q$.

** The calculated intensity of $N\rightarrow{}^1Q$ is uncertain because of the great uncertainty (cf. Table II, footnote 2) in the intensity of $N\rightarrow{}^3Q_1$. It would be very desirable that the latter should be measured quantitatively. There seems to be no doubt, however, that $N\rightarrow{}^3Q_1$ is much weaker than $N\rightarrow Q_0$.

TABLE IV. *Type I case c depressions of Q energy levels in* I_2. *The* H_{ii} *values are from Table II, those in brackets being calculated. The* $H_{\pi\pi}$ *and* $H_{\sigma\sigma}$ *estimates are based on Table III of reference 2. The* ρ *and* σ *values are calculated using Eqs. (23), (13), and the R values of Table III above. The* A_i*'s and* B_i*'s are then calculated following Eqs. (24), (25), (27) and (29), using* $a=5067$ *cm*$^{-1}$. *The* A_i *and* B_i *parts and the total* ΔE *are calculated according to Eqs. (29). The "observed"* ΔE *values for* $^3Q_1$ *represent the excess of the observed over the calculated value of the interval* $^3\Pi_{0^+}-{}^3\Pi_1$ *in Table III above.*

		DENOMINATORS (CM^{-1}×10^4)			PARAMETERS				CALCULATED ΔE (CM^{-1})			OBS. ΔE (CM^{-1})
		H_{ii}	$H_{\pi\pi}-H_{ii}$	$H_{\sigma\sigma}-H_{ii}$	ρ	σ	$A_i\times10^{-6}$	$B_i\times10^{-6}$	A_i PART	B_i PART	TOTAL	
$^3Q_1$	I	1.37	(2.28)	(3.25)	0.43	1.35	14.0	2.3	617	71	688	1680
	II	1.37	(2.28)	(3.25)	0.14	1.41	13.0	0.25	572	8	580	880
^1Q	I	[1.98]	(1.67)	(2.64)	0.43	1.35	23.6	23.1	1410	870	2280	—
	II	[1.89]	(1.76)	(2.73)	0.14	1.41	25.7	25.6	1460	940	2400	—
Q_0-		1.92	(1.73)	(2.70)			25.6	25.6	1470	950	2420	—

5510 ± 400 cm^{-1} from potential curve minima) is considerably larger than the calculated value for either of the interpretations I or II,—larger, indeed, than the value 5067 cm^{-1} corresponding to ideal Ω,ω coupling ($X=0$). This, like the high intensity of $N\rightarrow Q_0$ should be explainable by strong case *c* influences; a smaller effect of the same kind was noted above for bromine.

To investigate this matter more quantitatively we may use some of the equations of Section III. The predicted energy depressions ΔE of the levels $^3Q_1$, ^1Q, $Q_0(^3\Pi_{0^+u})$ and $Q_0{}^-(^3\Pi_{0^-u})$ by Type I case *c* influences are given approximately by

$$\begin{aligned}
&\Delta E(^3Q_1)\approx A_1/(H_{\pi\pi}-H_{11})+B_1/(H_{\sigma\sigma}-H_{11}),\\
&\Delta E(^1Q)\approx A_2/(H_{\pi\pi}-H_{22})+B_2/(H_{\sigma\sigma}-H_{22}),\\
&\Delta E(Q_0)=0,\\
&\Delta E(Q_0{}^-)=a^2/(H_{\pi\pi}-H_{33})+a^2/(H_{\sigma\sigma}-H_{33}).
\end{aligned}\tag{29}$$

These equations are based on Eqs. (24), (25) and (27), and the meaning of the A's and B's can be seen by referring to the latter and to Eqs. (23). In Eqs. (29), H_{11}, H_{22}, H_{33} refer to the energies which $^3Q_1$, ^1Q, and Q_0 would have in the absence of Type I case *c* perturbations, and $H_{\sigma\sigma}$ refers to the unperturbed energy of $\sigma\pi^4\cdot\sigma\pi^4$, $^3\Sigma_u{}^+$. The first term on the right-hand side of each of Eqs. (29) is a result of lumping together two terms in each of Eqs. (24)–(27). In each case, the denominators of both terms refer to odd states of the electron configuration $\sigma^2\pi^3\cdot\sigma^2\pi^3$; since these states are probably fairly close together in unperturbed energy, the latter may be replaced by an average value which we call $H_{\pi\pi}$, permitting lumping.

Table IV contains the numerical data necessary to calculate the ΔE's of Eq. (29) corresponding to each of the two interpretations I and II of Tables II and III for I_2. The most uncertain quantity used is $H_{\pi\pi}$ (compare the discussion in Section III); this quantity has been estimated from Table III of reference 2. The other quantities used are known or can be calculated fairly accurately. The "observed" ΔE's are simply the discrepancies between the actually observed $Q_0-{}^3Q_1$ energy interval and the intervals calculated corresponding to interpretations I and II without allowance for case *c* effects, and given in Table III.

Referring to the last two columns of Table IV, one sees that the "observed" and calculated ΔE values for $^3Q_1$ are of the same order of magnitude. The "observed" values are the larger, however, especially for interpretation I. This perhaps is evidence for interpretation II. Or, it may be taken to indicate that the actual quantities $H_{\pi\pi}-H_{ii}$ are smaller than the estimates in the table. It should, however, be kept in mind that some uncertainties are involved in identifying the figures in the last column with "observed" Type I case *c* depressions.

In any case it is clear from the Eq. (29) formulas and Table IV that the depressions of ^1Q and Q_0- must be much larger than those of $^3Q_1$.*

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* If the $H_{\pi\pi}-H_{ii}$ values are really much smaller than the estimates in Table IV, as is suggested by the comparison of observed and calculated ΔE's for $^3Q_1$, then the ΔE's for ^1Q and Q_0- become so large that Eqs. (25), (27) and (29) no longer form a good approximation, so that one should go back to the secular equations from which Eqs. (25) and (27) were obtained by expansion. In this case, our calculations of the $^1Q-{}^3Q_1$ interval and of the D_2/D_1 intensity ratio in Table III would need revision. The location of $N\rightarrow{}^3Q_1$, the conclusion that $N\rightarrow{}^1Q$ is weak and buried under $N\rightarrow Q_0$ with its $\nu_{\max}$ at smaller frequency than for the latter, and the conclusion that the ^1Q and Q_0- potential energy curves are below the Q_0 curve, would not be changed. However, there would now be very strong mixing of the

The position of $\nu_{\max}$ of $N \rightarrow {}^1Q$ as calculated in Table II must then certainly be lowered, making it definitely lower than $\nu_{\max}$ of $N \rightarrow Q_0$ by either of the interpretations I and II or any other within reason. The calculations therefore establish without much question that the ${}^1Q$ potential energy curve must throughout its course lie below the Q_0 curve. This removes a possibility of (spontaneous) predissociation which would otherwise be expected for Q_0 of I_2. In Br_2, the ${}^1Q$ curve probably cuts the Q_0 curve and so should cause predissociation (cf. Section IV). However, there seems to be a bare possibility even for Br_2 that ${}^1Q$ may run entirely below Q_0 as a result of case *c* depression (only, however, if interpretation II should be correct).

The calculations also leave little question that the $Q_0{}^-$ potential energy curve runs well below the Q_0 curve, and so cannot be the cause of the well-known magnetic predissociation observed in iodine.[6] This leaves the $\sigma^2\pi^3\cdot\sigma^2\pi^3$, ${}^1\Sigma_u{}^-$ and $({}^3\Sigma_u{}^+)_0{}^-$ curves, which should definitely intersect the Q_0 curve, as the cause of this phenomenon. This ansers a question left by Van Vleck when he analyzed this problem quantum-mechanically.†

VI. Toward Explanation of the $N \rightarrow Q_0$ Intensities

In Section III (cf. the discussion following Eq. (27), and that near Eq. (2)) two possibilities for explaining the high observed intensities of the $N \rightarrow Q_0$ transitions in the heavier halogens have been discussed. These will now be considered more quantitatively.

(1) If the strength of $N \rightarrow Q_0$ is determined mainly by perturbation of N by ${}^3\Pi_{0^+g}$, then for iodine

$$D_{NQ_0} \approx 0.03\left[\int \psi(Q_{0^+g})\Sigma z_i\psi(Q_0)d\tau\right]^2 = 0.03Q^2{}_{Q_gQ} = 0.03D_{Q_gQ}, \qquad (30)$$

where 0.03 is a value estimated in Section III following Eq. (28). The quantity Q_{Q_gQ} is found[17] to be given theoretically by the following:

AO approximation, $Q_{Q_gQ}=0$; *LCAO approximation*, $Q_{Q_gQ}=\frac{1}{2}r/(1-S_\pi{}^2)^{\frac{1}{2}}$. (31)

For iodine ($r_e=2.66$A, $S_\pi=0.09$, see reference 5), the LCAO expression gives $Q_{Q_gQ}=1.34$A, $D_{Q_gQ}=1.80\text{A}^2$. Hence by Eq. (30) we obtain the following values for D_{NQ_0} for iodine: zero by the AO approximation, 0.054A^2 by the LCAO approximation. The observed value (cf. Table II) is 0.061A^2. Since it is practically certain[17] that the true value of D_{Q_gQ} lies between the AO and LCAO values, more likely nearer the former in the present case, it appears probable that perturbation of N by Q_{0^+g} can account for only a part of the $N \rightarrow Q_0$ intensity.

(2) If, on the other hand, the strength of $N \rightarrow Q_0$ is determined mainly by perturbation of Q_0 by certain ionic states B, C, D, E as discussed in Section III, then we may write

$$\psi(Q_0)=a\psi_0(Q_0)-b\psi(B\ {}^1\Sigma_u{}^+)-c\psi(C\ {}^3\Sigma_u{}^-) -d\psi(D\ {}^1\Sigma_u{}^+)-e\psi(E\ {}^3\Pi_{0^+u})+\cdots. \qquad (32)$$

The wave function of each of the states B, C, D, E is a linear combination of the following type:

$$\psi_i=p_i\psi_0(\sigma^2\pi^4\cdot\sigma^2\pi^2,\ {}^1\Sigma_u{}^+) +q_i\psi_0(\sigma^2\pi^4\cdot\sigma^2\pi^2,\ {}^3\Sigma_u{}^-) +r_i\psi_0(\sigma^2\pi^4\cdot\pi^4,\ {}^1\Sigma_u{}^+) +s_i\psi_0(\sigma^2\pi^4\cdot\sigma\pi^3,\ {}^3\Pi_{0^+u}). \qquad (33)$$

${}^1Q$ with the $\sigma^2\pi^3\cdot\sigma^2\pi^3$, ${}^3\Delta_1$ and $({}^3\Sigma^+)_1$ wave functions, and weak transitions to the latter should occur, probably buried under $N \rightarrow Q_0$. Likewise, the wave functions of Q_0- and of $\sigma^2\pi^3\cdot\sigma^2\pi^3$, ${}^1\Sigma^-{}_u$ and $({}^3\Sigma^+{}_u)_0-$ would be strongly mixed. It is conceivable that the unperturbed energies of some of the states ${}^3\Delta_u$, ${}^3\Sigma_u{}^+$, ${}^1\Sigma_u{}^-$ of $\sigma^2\pi^3\cdot\sigma^2\pi^3$ might actually be *below* those of ${}^1Q$ and ${}^3Q_0-$, that is, $H_{\pi\pi}-H_{22}$ and $H_{\pi\pi}-H_{33}$ might be negative. But this is strongly improbable in view of Table III of reference 1. Also, this would increase the calculated ΔE's for ${}^3Q_1$ to values greater than those calculated in Table IV. Even if the possibility should be correct, it would mean such a strong mixing of wave functions that they could not well be identified any longer as ${}^1\Pi$, ${}^3\Delta_1$, ${}^3\Sigma^+$ and so on. There would merely be several states, some above and some below the Q_0.

† In case the Q_0- and the $\sigma^2\pi^3\cdot\sigma^2\pi^3$, ${}^1\Sigma_u{}^-$ and ${}^3\Sigma_u{}^+$ wave functions are strongly mixed (cf. footnote on p. 512) the question becomes more or less academic anyway.

[17] Cf. R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939), also reference 5, for methods of calculation. Intensity calculations for the type ${}^3\Pi_g \rightarrow {}^3\Pi_u$ have not been discussed previously, but the relation of the results of the two approximations to the true value of the dipole strength is doubtless similar to that for $\Sigma \rightarrow \Sigma$ and other parallel-type transitions previously treated. However, the precisely zero result for the AO approximation is a new feature. This result can be obtained by using expressions similar to Eqs. (24), (26) of reference 5—see text following these equations—for the ${}^3\Pi_{1g}$ and ${}^3\Pi_{1u}$ wave functions, and setting up

$$\int\psi^*({}^3\Pi_{1u})\Sigma z_i\psi({}^3\Pi_{1g})d\tau.$$

The result is the same for any component of the ${}^3\Pi$ states (${}^3\Pi_0$, ${}^3\Pi_1$, or ${}^3\Pi_2$)—also for ${}^1\Pi$.

The reason for the mixing of the unperturbed states ψ_0 of Eq. (33) is the existence of strong Type-I-case-c-like coupling among the unperturbed states, corresponding to partial persistence of atomic L, S, and J quantization. This is because all four ψ_0's correspond to the same atomic electron configuration $p^6 \cdot p^4$ (one negative and one positive ion). [For p^4 of the positive ion we have of course the states ^3P, ^1D, ^1S, partially mixed by partial J,j coupling.] It would not be difficult to set up the quartic secular equation for determining the coefficients in Eq. (33), but this would not be very useful, since it would contain several parameters whose values could be estimated only with much uncertainty.

Without the mixing indicated by Eq. (33), only the ionic $^3\Pi_{0^+u}$ would perturb Q_0. But because of the mixing of $\psi_0(^3\Pi_{0^+u})$ with the other three ψ_0's in Eq. (33), states B, C, D, E should all contain strong admixtures of $\psi_0(^3\Pi_{0^+u})$ and should therefore all perturb Q_0, as indicated in Eq. (32). Hence we have "Type II case c" mixing (cf. Section III) of (among others) $\psi_0(V)$ into Q_0, state V being the $\sigma^2\pi^4 \cdot \pi^4$, $^1\Sigma_u^+$ of Eq. (33).

Expanding Eq. (32) using Eq. (33) we have

$$\psi(Q_0) = \alpha\psi_0(Q_0) - \beta\psi_0(^3\Pi_{0^+u}) - \gamma\psi_0(V\,^1\Sigma_u^+) + \cdots, \quad (34)$$

where

$$\gamma = br_B + cr_C + dr_D + er_E. \quad (35)$$

Of the several r_i's, two may be opposite in sign to the other two, so that γ might be small even if the coefficients in Eqs. (32) and (33) are all numerically relatively large. We shall return to this shortly.

From Eq. (34), the dipole strength of $N \rightarrow Q_0$ due to admixture of $\psi_0(V)$ into $\psi_0(Q_0)$ is readily seen to be

$$D_{NQ_0} = \gamma^2 \left[\int \psi(N) \Sigma z_i \psi_0(V) d\tau \right]^2 = \gamma^2 D_{NV}. \quad (36)$$

If the observed intensity of $N \rightarrow Q_0$ is due to this cause, then the observed D values for $N \rightarrow Q_0$ of Cl_2, Br_2, and I_2 (Table II, column 7 or 10) can be used to evaluate $|\gamma|$, provided we know the D values for the $N \rightarrow V$ transitions. These have been calculated theoretically for each of two approximations (AO and LCAO) in a previous paper.[18] It seems likely[18] that the true D values are intermediate between those calculated by the two methods. The necessary D values and the resulting calculated $|\gamma|$ values are given in Table V.

TABLE V. *Perturbation of state Q_0 by state V. The observed $D(N \rightarrow Q_0)$ values are from Table II; for* Br_2, *an average of the values from the two interpretations has been used. The D values are in A^2. For the calculated D_{NV} values, see reference 18.*

MOLECULE	OBS. $D(N \rightarrow Q_0)$	CALC. D_{NV}		CALC. $\|\gamma\|$	
		AO	*LCAO*	*AO*	*LCAO*
Cl_2	0.0001	0.35	1.96	0.02	0.01
Br_2	0.003	0.63	2.60	0.07	0.03
I_2	0.061	1.09	3.53	0.24	0.13

We may now inquire whether the $|\gamma|$ values indicated by Table V can be understood by the Type II case c mechanism proposed above. According to perturbation theory, we have for b in Eq. (32):

$$b = \left[\int \psi_0(Q_0) H \psi(B) dv \right] / (H_{BB} - H_{Q_0Q_0}), \quad (37)$$

with similar relations for c, d, e. Here H_{BB} and $H_{Q_0Q_0}$ are the energies of states B and Q_0 before considering their mutual perturbation. According to the preceding discussion, the integral H_{Q_0B} in Eq. (37) would vanish if it were not for the term $s_B\psi_0(^3\Pi_{0^+u})$ in Eq. (33) for ψ_B. Hence

$$H_{Q_0B} = s_B \int \psi_0(Q_0) H \psi_0(\sigma^2\pi^4 \cdot \sigma\pi^3, {}^3\Pi_{0^+u}) d\tau = s_B H_{Q_0R}. \quad (38)$$

If one uses Eqs. (37), (38) and analogous equations, he finds Eq. (35) becomes

$$\gamma = H_{Q_0R} \sum_i r_i s_i / (H_{ii} - H_{Q_0Q_0}), \quad (39)$$

where $i = B, C, D, E$.

For I_2, $|\gamma|$ is about 0.2 according to Table V. To see whether this could be reproduced by Eq. (39), let us consider the hypothetical case $r_B s_B = r_E s_E = 0.4$, $r_C s_C = r_D s_D = 0$, with $H_{BB} - H_{Q_0Q_0} = 3$ ev, $H_{EE} - H_{Q_0Q_0} = 6$ ev. To obtain $|\gamma| = 0.2$, we then require $H_{Q_0R} = 3.0$ ev, which, while

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[18] Cf. R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939), Table III. The relation $D = 0.912 \times 10^5 f/\nu$ (for D in A^2) holds between the f values given there and the D values desired here.

large, might not be impossible. Thus it seems possible that the observed intensities of $N\rightarrow Q_0$ might be explained by the mechanism discussed. Our hypothetical case, however, has had to be forced about to the limits of credibility in every direction in order to match the observed $|\gamma|$, so that it remains doubtful whether the actual $N\rightarrow Q_0$ intensities are really explainable in this way. Nevertheless, it is difficult to see what other mechanisms than the one here discussed and that considered at the beginning of this section could be responsible to an important extent for the $N\rightarrow Q_0$ intensities. We may then probably conclude that these two mechanisms are the ones mainly responsible.

VII. Mixed Halogens

In the mixed halogen molecules, e.g. ICl, there are *two* Q complexes and *two* $N\rightarrow Q$ complexes. Really, there are also two in the homopolar halogens, but the higher energy Q complex is $^{1,3}\Pi_g$ and transitions to it from N are rigorously forbidden. For ICl, there exist absorption coefficient curves for the continua corresponding to both the high frequency and the low frequency Q complex.[2] In both cases, the curve has a single maximum, with no definite evidence of shoulders to indicate weak subsidiary peaks. It is, therefore, hardly possible to make analyses like those of Sections IV and V.

The long wave-length $N\rightarrow Q$ ICl continuum is accompanied by $N\rightarrow {}^3Q_1$ and $N\rightarrow Q_0$ bands. According to information from Professor W. G. Brown, it is likely that $N\rightarrow Q_0$ is the stronger, and so that the observed continuum is mainly $N\rightarrow Q_0$. $\Sigma G'D$ is roughly $86\times10^{-4}\text{A}^2$. This interpretation involves certain difficulties, however, when analysis based on Section II is applied. A careful remeasurement of the absorption coefficient curve, with a foreign gas to suppress band structure, and an analysis according to the methods used by Gibson, Bayliss, and collaborators for Cl_2 and Br_2, would be very interesting. Such an analysis might help in deciding between the two alternative interpretations proposed for Br_2 and I_2 in the preceding sections. Further work on IBr and BrCl would also be interesting.

The writer is inclined to interpret the high frequency $N\rightarrow Q$ continuum of ICl, with $\Sigma G'D$ roughly $112\times10^{-4}\text{A}^2$, as essentially $N\rightarrow Q_0$. Or possibly the transition is not $N\rightarrow Q$ at all.

VIII. The λ2250 Bromine Continuum

In addition to the $N\rightarrow Q$ spectra, and the $N\rightarrow V$ and other spectra below λ2000, bromine shows absorption between λ2000 and the visible. According to Aickin and Bayliss, this is weak in the vapor, but is very sensitive to pressure and (according to various observers) becomes strong in liquid and solution.[19] According to Aickin and Bayliss, the vapor spectrum consists of an absorption continuum with maximum near λ2250A and a total dipole strength ($\Sigma G'D$) about 0.013 as great as that of the region of the A and B peaks, together with possible indications of bands.

There are various possible transitions for explaining this absorption (cf. reference 2, Table III). Only one such transition is allowed for Λ,S coupling. This is expected to be weak. Its upper level is $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$, $^1\Sigma_u^+$ by MO's, $\sigma^2\pi^4\cdot\sigma^2\pi^2$ by AO's, and is expected to be a stable level. Transitions to this level might account for weak bands.

Other transitions are allowed only by reason of case c effects in Ω,ω coupling; these go to certain 0_u^+ and 1_u case c states, especially the 1_u states involved in Eq. (22). One or more of these transitions may account for the λ2250 continuum. In particular, the upper level of the λ2250 continuum may be the $T\,{}^3\Sigma_u^+$ state,[5] of electron configuration $\sigma_g\pi_u^4\pi_g^4\sigma_u$ by MO's, $\sigma\pi^4\cdot\pi^4\sigma$ by AO's. If this is perturbed by the ^1Q level in accordance with Eq. (22), a simple perturbation calculation shows that the dipole strength of the transition $N\rightarrow T$ should be about 0.03 times that of $N\rightarrow {}^1Q$. This is in rough agreement with the observed dipole strength of the λ2250 continuum.

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[19] See R. G. Aickin and N. S. Bayliss, Trans. Faraday Soc. **34**, 1371 (1938) for quantitative vapor data and references to earlier work; R. G. Aickin, N. S. Bayliss and A. L. G. Rees, Proc. Roy. Soc. **A169**, 234 (1938) for their solution work and for other references.