Table III. Average Fluorine Chemical Shifts and Spin-Coupling Constants of Group V Fluoride Species[a]

Element	$\delta(MF_5)$	$\delta(MF_6^-)$	$\Delta\delta$	MNF_{11}^- δ_1	δ_2	δ_3	J_{1-2}	J_{1-3}	J_{2-3}
P	65.8[5]	71.0[5]	5.2						
As	57.0[5]	61.7[5]	4.7	89[5]	56[5]	21.1[4]	127[5]	0[5]	49[5]
Sb	106.7[3]	117.9[3]	11.2	143[5]	115[5]	92[3]	96[5]	0[5]	57[5]
Nb	−162	−104	58	−192	−147	56	41	179	41
Ta	−99.6	−40.4	59.2	−116	−73	81	23	171	43

[a] δ values in ppm; *J* values in Hz.

(TBA)Ta_2F_{11}, 37534-34-2; NbF_5, 7783-68-8; (TBA)NbF_6, 37477-93-3; (TBA)Nb_2F_{11}, 37477-94-4; (TBA)$TaNbF_{11}$, 37534-35-3; (TBA)$TaSbF_{11}$, 37477-95-5; (TBA)$NbSbF_{11}$, 37477-96-6; (TBA)$TaAsF_{11}$, 37477-97-7.

Acknowledgments. The author wishes to thank Mr. J. Bornais for some of the fluorine resonance spectra, Mr. G. Latremouille for sample preparations, and Dr. L. Calvert for the X-ray diffraction photographs.

Contribution from the Inorganic Chemistry Laboratory,
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Semiempirical Molecular Orbital Calculation of Symmetrical Trihalide Ions

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Received August 15, 1972

The $\sigma_u^* \leftarrow \sigma_g$ electronic transitions of symmetrical trihalide ions (I_3^-, IBr_2^-, ICl_2^-, Br_3^-, and $BrCl_2^-$) are calculated in a molecular orbital approximation. The MO's are formed from linear combinations of $np\sigma$ halogen orbitals. For the zero-order calculations a modified Huckel theory is used. The calculations of the electronic transitions in the σ system are refined by configuration interaction with complete neglect of differential overlap. The parameters β for the σ bonds are based on the experimental electronic transitions of Br_2, Cl_2, and I_2. The method is applied to one transition of the I_3^- ion (4.25 eV) in order to obtain an equation for β. The agreement between the calculated values and the experimentally observed transitions appears to be a good one. A table of calculated charges and bond orders is also presented.

Introduction

For trihalide ions the bonding scheme of Pimentel[1] is generally accepted.[2-7] The bonds are formed from overlap of the $np\sigma$ orbitals of the constituting atoms (Figure 1). Molecular orbitals for the σ system can be formed from linear combinations of these $np\sigma$ halogen orbitals

$$\phi_i = \sum_\mu c_{\mu i}\chi_\mu \quad (\phi_i, \phi_j\text{: MO; } \chi_\mu, \chi_\nu\text{: AO})$$

Three MO's result from this combination, two of which are doubly occupied. In a Huckel-type calculation these orbitals are bonding and formally nonbonding, respectively (Figure 2). The p_X and p_Y orbitals of all atoms are each occupied by two electrons. The *n*s orbitals at each atom, which are much lower in energy than the *n*p orbitals,[1,6] are also occupied by two electrons. In this way the total of valence electrons is 22. The only empty orbital is an antibonding one and has the σ_u symmetry (Figure 2). The p_X and p_Y orbitals are regarded as nonbonding, although in practice there will be a splitting in slightly bonding, nonbonding, and slightly antibonding orbitals, due to some interaction. The total energy of the σ electrons in a Huckel-type calculation is

$$E_{\text{tot}} = 2\sum_i^{\text{occ}}\sum_\mu\sum_\nu c_{\mu i}{}^*c_{\nu i}\int \chi_\mu{}^*(1)\hat{H}_{\text{eff}}(1)\chi_\nu(1)\,d\tau = \sum_\mu P_{\mu\mu}H_{\mu\mu} + 2\sum_{\mu>\nu} P_{\mu\nu}H_{\mu\nu} \tag{1}$$

in which $\Sigma_i{}^{\text{occ}}$ denotes the summation over the occupied molecular orbitals, $P_{\mu\nu} = 2\Sigma_i c_{\mu i}{}^*c_{\nu i}$ is the bond order, and $\hat{H}_{\text{eff}}$ is the one-electron Huckel Hamiltonian operator.

Wiebenga and Kracht[4] replaced the term $\Sigma_\mu P_{\mu\mu}H_{\mu\mu}$ by $\Sigma_A E_A + \Sigma_{A>B} Q_A Q_B/R_{AB}$, in which $\Sigma_A E_A$ denotes the self-energy of the atoms in the trihalide ions ($\Sigma_A E_A$ is a summation over the atoms) and $\Sigma_{A>B} Q_A Q_B/R_{AB}$ denotes the Coulomb repulsions between the net charges on the atoms; Q_A is the net charge on atom A and R_{AB} is the intraionic distance between atoms A and B in the trihalide ion.

E_A can be deduced from the ionization potential (I_A) and the electron affinity (A_A) of atom A. The ion A^- has the energy $-A_A$, A^+ has the energy $+I_A$, and the neutral atom has the energy zero. Between these values the energy can be approximated by a parabolic function (Figure 3).[4] In order to get the zero-order MO's, the total energy, modified in this way, must be minimized. In the present case, with only one basis function per atom, and neglecting differential overlap, the matrix elements that occur are

$$\begin{aligned} F_{\mu\mu} &= -{}^1\!/_2(I_A + A_A) - (I_A - A_A)Q_A - \sum_{B\neq A}\frac{Q_B}{R_{AB}} \quad \mu \in A \\ F_{\mu\nu} &= H_{\mu\nu} = \beta \end{aligned} \tag{2}$$

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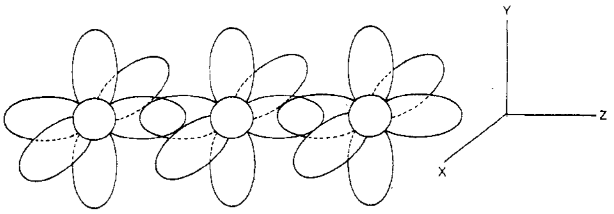

Figure 1. Bond formation in trihalide ions by overlap of the $np\sigma$ atomic orbitals.

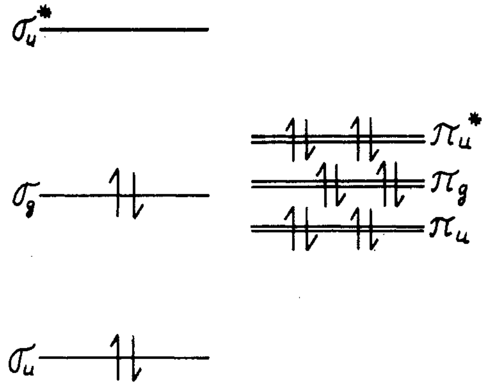

Figure 2. Molecular orbitals in trihalide ions.

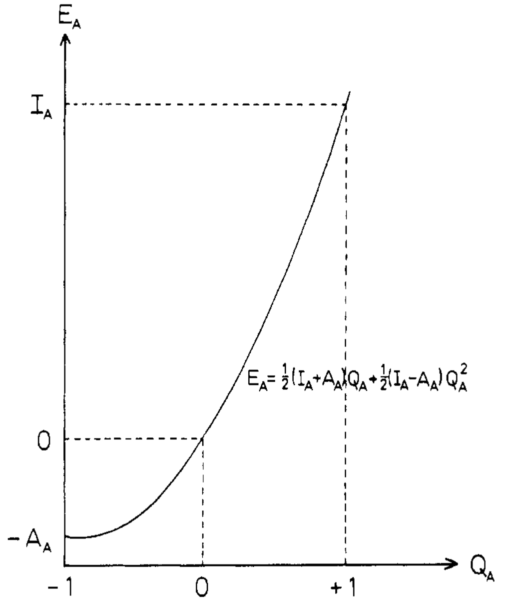

Figure 3. Parabolic approximation of the self-energy of the atoms.

The procedure is an iterative one, because the charges Q are unknown at the beginning. The quantities I_A and A_A for I, Br, and Cl have been taken from literature[8] and the distances R_{AB} in the trihalide ions have been taken from crystallographic determinations[9-15] (see also Table I). The parameters β are discussed in the next section. After the calculation of the zero-order MO's, the transition energies of the singlet-singlet and singlet-triplet transitions are calculated using complete configuration interaction, assuming complete neglect of differential overlap. For this reason, calculation of the two-electron repulsion integrals between atomic orbitals is necessary.

Derivation of the Parameters β

The parameters β in eq 2 are empirically determined from the known electronic transitions of some diatomic halogen molecules and from the electronic transition of one trihalide ion, for calibration. In this paper I_3^- is used for this calibration.

The vertical energy for the $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition for I_2 can be calculated from the experimental ν_e value[16] and the dissociation energy of the excited molecule,[16] with the aid of the Morse potential.[17] The vertical energy calculated in this way is 6.48 eV (Figure 4). The best fit between theoretical and experimental transition energy results in a $\beta(I_2)$ value of -2.551 eV. The calculation has been carried out including configuration interaction.

In the same way the parameter β for the σ-σ bonds in I_3^- can be calculated from the experimental electronic transition energy for this ion (4.25 eV).[9,18-21] The result is a β value of -2.237 eV (including configuration interaction; see next section). Assuming a linear relationship of β with the length R in a bond (Figure 5), as is supposed by Wiebenga and Kracht,[4] eq 3 can be deduced from the two known β's

$$\beta(R) = 1.190(R - R_{\text{cov}}) - 2.551 \tag{3}$$

(Figure 5).

In this paper the value 1.190 from (3) is used for all other interhalogen bonds in symmetrical XY_2^- ions, with X, Y = Cl, Br, I. See eq 4, in which R is the distance of the inter-

$$\beta = 1.190(R - R_{\text{cov}}{}^{XY}) + \beta_{XY} \tag{4}$$

halogen bond in a symmetric trihalide ion, $R_{\text{cov}}{}^{XY}$ is the distance in the diatomic XY molecule, and β_{XY} is the empirically determined parameter for the diatomic molecule. For Br_2 and Cl_2, β can be calculated in the same way as for I_2, from the electronic transition energies. These last energies have been determined by Asundi and Venkateswarlu.[16] In this paper these values are raised by 6.2% in analogy to the correction which was necessary for I_2 in order to get the desired vertical energy.

For IBr, ICl, and BrCl the β's are taken as the average values of $\beta(I_2)$ and $\beta(Br_2)$, etc., respectively.

Derivation of the Repulsion Integrals

For calculations including configuration interaction, atomic repulsion integrals are necessary. Because of the semiempirical description of the trihalide ions in this paper, it is justified to maintain the approximation of complete neglect of differential overlap. In this way only three kinds of atomic repulsion integrals remain to be determined.

(1) $\gamma_{\mu\mu}$, Repulsion Integrals between Atomic Orbitals at the Same Atom. For these integrals the experimental value $I_A - A_A$ (the ionization potential of atom A minus its electron affinity) is chosen, according to theoretical considerations of Pariser.[8,22]

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Table I. Parameters Used for the Semiempirical Description[a]

	Vertical energy	β	R	R_{cov}	$R_W{}^3$	γ
I_2	6.48^{16}	-2.551^b	2.666^3	2.666^3	4.30	$\gamma_{11} = \gamma_{22} = 7.32, \gamma_{12} = 4.86$
Br_2	6.90^{16}	-2.674^b	2.284^3	2.284^3	3.90	$\gamma_{11} = \gamma_{22} = 8.41, \gamma_{12} = 5.65$
Cl_2	7.65^{16}	-2.999^b	1.988^3	1.988^3	3.60	$\gamma_{11} = \gamma_{22} = 9.33, \gamma_{12} = 6.39$
IBr		−2.612				
ICl		−2.775				
BrCl		−2.836				
I_3^-	$4.25^{9,18-21}$	-2.237^b	$2.93^{10-12,15}$	2.666^3	4.30	$\gamma_{11} = \gamma_{22} = \gamma_{33} = 7.32, \gamma_{12} = \gamma_{23} = 4.61, \gamma_{13} = 2.46$
IBr_2^-		−2.380	2.67^9	$2.475^{3,9}$	4.10	$\gamma_{11} = \gamma_{33} = 8.41, \gamma_{22} = 7.32, \gamma_{12} = \gamma_{23} = 5.03, \gamma_{13} = 2.70$
ICl_2^-		−2.557	2.51^9	$2.327^{3,9}$	3.95	$\gamma_{11} = \gamma_{33} = 9.33, \gamma_{22} = 7.32, \gamma_{12} = \gamma_{23} = 5.35, \gamma_{13} = 2.87$
Br_3^-		−2.369	$2.54^{13,14}$	2.284^3	3.90	$\gamma_{11} = \gamma_{22} = \gamma_{33} = 8.41, \gamma_{12} = \gamma_{23} = 5.34, \gamma_{13} = 2.83$
$BrCl_2^-$		−2.558	2.37^9	$2.136^{3,9}$	3.75	$\gamma_{11} = \gamma_{33} = 9.33, \gamma_{22} = 8.41, \gamma_{12} = \gamma_{23} = 5.69, \gamma_{13} = 3.08$

[a] For I, $I_A = 10.45, A_A = 3.13$; for Br, $I_A = 11.84, A_A = 3.43$; for Cl, $I_A = 13.01, A_A = 3.68$.[8] Vertical energy, β, γ, I_A, and A_A in eV; R, R_{cov}, and R_W in Å. [b] Basic parameters, from experimental transition energies.

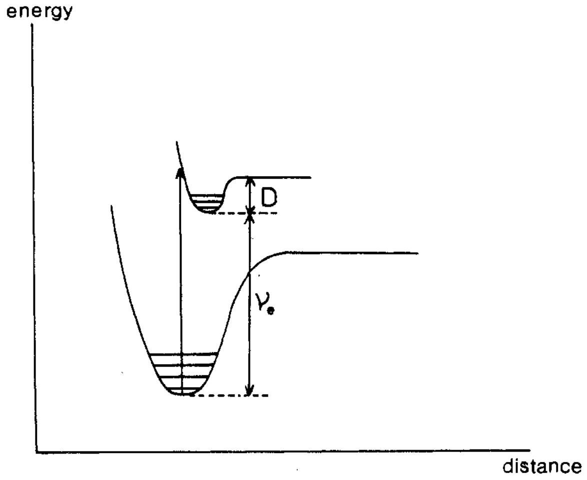

Figure 4. Vertical energy of the ${}^1\Sigma_u{}^+ \leftarrow {}^1\Sigma_g{}^+$ electronic transition in the I_2 molecule: ${}^1\Sigma_g{}^+$, lower curve; ${}^1\Sigma_u{}^+$, upper curve.

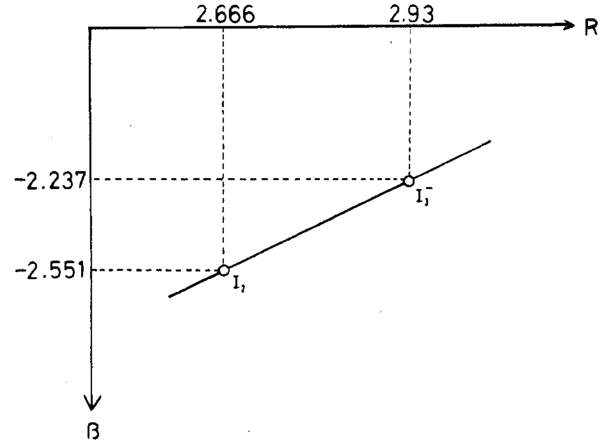

Figure 5. Linear relationship between β and distance R.

(2) $\gamma_{\mu\nu}$, **Repulsion Integrals between Atomic Orbitals at Two Different and Not Adjacent Atoms.** These integrals are approximated by the point charge model, $\gamma_{\mu\nu} = 14.4/R$ in which the factor 14.4 is for getting the γ values in electron volts.

(3) $\gamma_{\mu\nu}$, **Repulsion Integrals between Atomic Orbitals at Two Adjacent Atoms.** These integrals are approximated by a kind of interpolation between the cases 1 and 2, according to the method described by Migchelsen for the I_3^- ion[10] (Figure 6). The point charge model of case 2 is used for two atoms if they are separated from each other by an intraatomic distance of at least the sum of their van der Waals radii (R_W). Between the points $\gamma_{\mu\mu}$ (repulsion integrals at one atom) and $14.4/R_W$ (starting point of the point charge model) the desired γ values for two adjacent atoms can be found by a linear interpolation. If the bond is formed by two different atoms (IBr_2^-, ICl_2^-, and $BrCl_2^-$) there are two values for $\gamma_{\mu\mu}$. Before the interpolation these values are averaged.

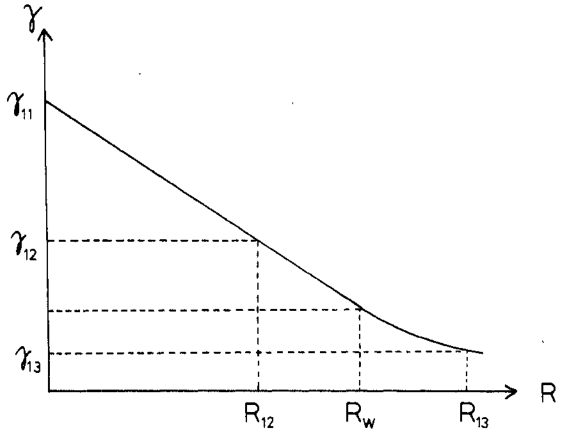

Figure 6. Atomic repulsion integrals.

Calculation of the Basic β Values

The calculation of the β values from the electronic transition energies for I_2, Br_2, and Cl_2, including configuration interaction, is straightforward and simple. The zero-order MO's are completely determined by the symmetry of the system. Configuration interaction results in a quadratic equation in β, which can be solved very easily.

The calculation of the β value for I_3^- is more difficult. The procedure used is a trial and error method followed by an iterative process. With a guessed value of β eq 2 are solved in an iterative way until self-consistency for the charges Q is attained. With the resulting zero-order MO's complete configuration interaction calculations are carried out. The resulting theoretical transition energy is compared with the experimental one. If this procedure is repeated for a range of β values, the best fit of β can be obtained by interpolation from a graph of β *vs.* transition energy (Figure 7).

Configuration Interaction

The matrix elements between four-electron determinantal configurations are known in the literature and have been used for the calculations in this paper.[23]

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Table II. Calculated Properties for the Trihalide Ions

	Singlet-singlet transition		Singlet-triplet transition		Charges		
	Exptl	Calcd	Exptl	Calcd	$Q_1 = Q_3$	Q_2	Bond order, P_{12}
I_3^-	4.25	4.25[a]	2.71	2.65	−0.493	−0.014	0.691
IBr_2^-	4.80	4.87	3.25	3.15	−0.531	+0.062	0.691
ICl_2^-	5.42	5.50	3.52	3.69	−0.558	+0.115	0.688
Br_3^-	4.57	4.56	3.05	2.79	−0.494	−0.013	0.689
$BrCl_2^-$	5.15	5.17	3.45	3.29	−0.523	+0.046	0.690

[a] Value used for calibration of β.

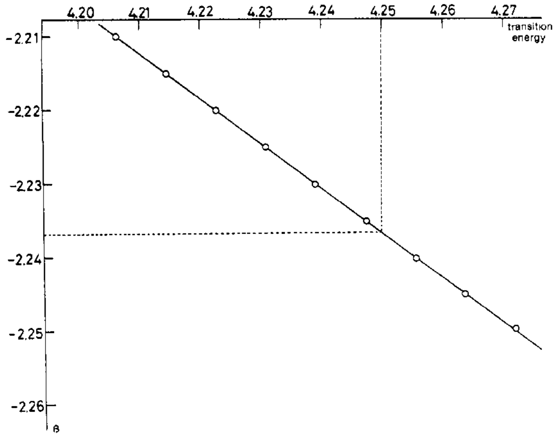

Figure 7. Theoretical transition energy as a function of β.

The Hamiltonian operator can be written as[23,24]

$$\hat{H} = \sum_i \hat{H}_{\text{core}}(i) + \sum_{i>j} \frac{e^2}{r_{ij}} \tag{5}$$

All matrix elements can be expressed in core integrals of the type[23,24]

$$I_{ij} = \int \phi_i^*(1) \hat{H}_{\text{core}}(1) \phi_j(1)\, d\tau \tag{6}$$

and electronic repulsion integrals of the type[23,24]

$$(ij|kl) = \int \phi_i^*(1)\phi_j(1) \frac{e^2}{r_{12}} \phi_k^*(2)\phi_l(2)\, d\tau \tag{7}$$

The core integrals I_{ij} can be reduced further[23,24]

$$I_{ij} = \sum_{\mu}\sum_{\nu} c_{\mu i}^* c_{\nu j} H_{\mu\nu}^{\text{core}} \tag{8}$$

where

$$H_{\mu\nu}^{\text{core}} = \int \chi_\mu^*(1) \hat{H}_{\text{core}}(1) \chi_\nu(1)\, d\tau \tag{9}$$

The coefficients $c_{\mu i}$, $c_{\nu j}$ are determined in the zero-order Huckel calculation; the integral $H_{\mu\nu}^{\text{core}}$ equals β for atomic orbitals χ_μ and χ_ν on adjacent atoms; otherwise it is zero.

In the case $\mu = \nu$ the integral $H_{\mu\mu}^{\text{core}}$ is called the Coulomb integral. It represents the sum of the kinetic energy of an electron in orbital μ, the potential energy of this electron with regard to its own core ion, and the potential energy of this electron with regard to the other ions in the core

$$H_{\mu\mu}^{\text{core}} = \int \chi_\mu^*(1)\{\hat{T}(1) + \hat{U}(1)\}\chi_\mu(1)\, d\tau + \sum_{\nu \neq \mu} \int \chi_\mu^*(1) \hat{U}(\nu) \chi_\mu(1)\, d\tau \tag{10}$$

in which $\hat{T}(1)$ denotes the kinetic energy operator, $\hat{U}(1)$ denotes the potential energy operator for electron 1 with regard to its own ion in the core, and $\hat{U}(\nu)$ denotes the potential energy operator with regard to ion ν in the core.

The first part of eq 10 is taken as the negative ionization potential of the atomic orbital χ_μ,[25] while the second part is approximated by the negative σ-σ repulsion integrals,[26] which were derived in an earlier section

$$H_{\mu\mu}^{\text{core}} = -I_A - \sum_{\nu \neq \mu} \gamma_{\nu\mu} \quad \mu \in A \tag{11}$$

Calculated Transition Energies, Charge Distributions, and Bond Orders

Table II contains the calculated properties of the ions. The energies for the singlet-singlet transitions have been known for years. The values mentioned in the table are taken from literature.[9,19-21] The singlet-triplet transitions are not known so far and will be published.[18]

Conclusions

It has been pointed out that the experimental electronic transition energies for symmetrical trihalide ions can be predicted from theoretical calculations.

For the σ system a minimum basis set is sufficient to obtain agreement between theoretical and experimental values of these transition energies. The empirical relationship between the β values of I_2 and I_3^-

$$\beta = 1.190(R - R_{\text{cov}}) + \beta_{I_2}$$

may also be used for the other trihalide ions.

The neglect of π-σ interaction for the trihalide ions, which is very common for calculations for unsaturated hydrocarbons, has no consequences.

Registry No. I_3^-, 14900-04-0; IBr_2^-, 14791-49-2; ICl_2^-, 14522-79-3; Br_3^-, 14522-80-6; $BrCl_2^-$, 14522-78-2.

Acknowledgment. We wish to thank Dr. S. de Bruyn (Institute for Theoretical Chemistry, University of Amsterdam) for reading the manuscript for this article and his advice during the calculations. We are very grateful to Miss. Ch. Oudshoorn for checking our calculations and testing the influence of the choice of the parameters on the final result.

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