On the Electron Affinity of Fluorine

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The hamiltonian for systems isoelectronic with neon is treated by perturbation methods. The energy of ionization of such systems is represented by a four-term expression (i.e., to third order of perturbation); the two leading terms are calculated, spectroscopic data for isoelectronic systems are used to evaluate the constants in the two remaining terms. The electron affinity of fluorine is estimated to be 73±3 kcal/g atom. The corresponding dissociation energy of fluorine, as inferred by the Born-Haber cycle, is estimated to be 18 kcal/mole, to an accuracy believed better than ±12 kcal/mole.

PRINCIPLE OF THE CALCULATION[1]

CHOOSING as the unit of mass the reduced mass of an electron with respect to its atomic system, and taking the electronic charge to be of unit magnitude, then the hamiltonian for the relative motion of n point electrons, about a point nucleus of charge Z, may be written as $H+H'$ where

$$H = \sum_i \left[\tfrac{1}{2} p_i^2 - (Z-S) r_i^{-1} \right]$$

and

$$H' = \sum_{i<j} \left[r_{ij}^{-1} - \epsilon p_i \cdot p_j \right] - \sum_i S r_i^{-1}.$$

Herein ϵ denotes the reciprocal of the atomic mass, and the shielding constant S is a separation artifice. H' is regarded as a perturbation on the exactly soluble system. Setting Planck's constant equal to 2π, and adopting the second as the unit of time, completes the definition of units.

Let $u_j(i)$ denote the unperturbed wave function of the jth electron having quantum numbers n^i, l^i, m^i, and s^i.

Let

$$\phi(A) = (n!)^{-\frac{1}{2}} \begin{vmatrix} u_1(a) & \cdots & u_n(a) \\ u_1(c) & \cdots & u_n(c) \\ u_1(d) & \cdots & u_n(d) \\ u_1(n) & \cdots & u_n(n) \end{vmatrix}.$$

Let

$$\phi(B) = (n!)^{-\frac{1}{2}} \begin{vmatrix} u_1(\alpha) & \cdots & u_n(\alpha) \\ u_1(\nu) & \cdots & u_n(\nu) \end{vmatrix},$$

and suppose that several rows of $\phi(B)$ appear also in $\phi(A)$, though they need not be corresponding rows. By $\phi(B')$ is denoted the expression derived by permuting the rows of $\phi(B)$ so that rows common to $\phi(B)$ and $\phi(A)$ are in corresponding positions.

Thus

$$\phi(B') = (n!)^{-\frac{1}{2}} \begin{vmatrix} u_1(a) & \cdots & u_n(a) \\ u_1(\gamma) & \cdots & u_n(\gamma) \\ u_1(\delta) & \cdots & u_n(\delta) \\ u_1(n) & \cdots & u_n(n) \end{vmatrix},$$

which is row for row identical with $\phi(A)$, except that rows $u_1(\gamma) \cdots u_n(\gamma)$, $u_1(\delta) \cdots u_n(\delta)$, etc., differ from $u_1(c) \cdots u_n(c)$, $u_1(d) \cdots u_n(d)$, etc., as they must since they pertain to quantum numbers not common to $\phi(B)$ and $\phi(A)$. Clearly,

$$\phi(B) = (-1)^t \phi(B'),$$

where t denotes the number of interchanges required to bring $\phi(B)$ to $\phi(B')$.

The perturbation is seen to consist of terms of type $G = \sum_{i<j} g_{ij}$ and of type $F = \sum_i f_i$. Slater's treatment[1] shows that[2]

$$\begin{aligned} (A/G/B) &= \sum_{c<d} \left[(cd/g/cd) - (cd/g/dc) \right] \text{ if } \phi(B') = \phi(A) \\ &= (-1)^t \sum_c \left[(cd/g/c\delta) - (cd/g/\delta c) \right] \text{ if } \phi(B') \\ &\quad \text{and } \phi(A) \text{ differ by one row } (\delta \neq d) \\ &= (-1)^t \left[(cd/g/\gamma\delta) - (cd/g/\delta\gamma) \right] \text{ if } \phi(B') \text{ and} \\ &\quad \phi(A) \text{ differ by two rows } (\gamma \neq c; \delta \neq d) \\ &= 0 \text{ if } \phi(B') \text{ and } \phi(A) \text{ differ by more than two rows.} \end{aligned}$$

$$\begin{aligned} (A/F/B) &= \sum_c (c/f/c) \text{ if } \phi(B') = \phi(A) \\ &= (-1)^t (d/f/\delta) \text{ if } \phi(B') \text{ and } \phi(A) \text{ differ by one row } (\delta \neq d) \\ &= 0 \text{ if } \phi(B') \text{ and } \phi(A) \text{ differ by more than one row.} \end{aligned}$$

Since L_z, L^2, S_z, and S^2 commute with the hamiltonian, the wave functions may be chosen to be single expressions of the type $\phi(A)$.

The energy of the ground state is given (to third order of Rayleigh-Schroedinger perturbation) by

$$E \cong H_{00} + H_{00}' + \sum_k' \frac{H_{0k}' H_{k0}'}{H_{00} - H_{kk}}$$

$$+ \left[\sum_k' \sum_n' \frac{H_{0k}' H_{kn}' H_{n0}'}{(H_{00} - H_{kk})(H_{00} - H_{nn})} - H_{00}' \sum_k' \frac{H_{0k}' H_{k0}'}{(H_{00} - H_{kk})^2} \right] \quad (1)$$

where the subscript $_0$ refers to the ground state, while

[1] Development follows as closely as possible notation of E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935).

[2] $(A/G/B) \equiv \int \cdots \int \phi^*(A) G \phi(B) d\tau_1 \cdots d\tau_n$ and $(cd/g/\gamma\delta)$
$= \sum_{s_1} \sum_{s_2} \int\int\int\int\int\int u_1^*(n^c, l^c, m^c, s^c) u_2^*(n^d, l^d, m^d, s^d)$
$\times g_{12} u_1(n^\gamma, l^\gamma, m^\gamma, s^\gamma) u_2(n^\delta, l^\delta, m^\delta, s^\delta) d\tau_1 d\tau_2$ etc., after the Dirac notation.

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subscripts $_k$ and $_n$ refer to excited states. It is proposed to estimate the difference in energies between systems in the $1s^2 2s^2 2p^6$, $^1S_0$ state, and the corresponding systems with an electron removed, in the $1s^2 2s^2 2p^5$, $^2P_{\frac{3}{2}}$ state, by use of this expression. (The configurations $1s^2 2s^2 2p^5$ and $1s^2 2s 2p^6$ are degenerate in the unperturbed system; this leads to no complication, however, since these configurations are of opposite parity, while H' is of even parity.) The summations are assumed to converge. Since $\epsilon \ll 1$, contributions from the term $\epsilon \sum_{i<j} p_i \cdot p_j$ are neglected.

For all members of an isoelectronic sequence the various terms in the Rayleigh-Schroedinger expression (1) will differ only by powers of the scale factor $(Z-S)$. Specifically, the energy of any member of an isoelectronic sequence, having nuclear charge Z, is given by an expression of the form,

$$E(Z) \cong A(Z-S)^2 + B(Z-S) + C + D(Z-S)^{-1}, \quad (2)$$

where A, B, C, and D (all of which, of course, pertain to the same specific electronic configuration) are finite and independent of Z, and pertain to perturbation contributions of orders zero through three, respectively.

In the simplest of variation treatments, the energy of an atomic system is estimated using, as trial function, an antisymmetric function composed of products of hydrogenic functions for the individual electrons; and the nuclear charge is regarded as the parameter of variation. The first-order perturbation treatment of this paper, with optimum choice of S, is equivalent to such a variation calculation. In the variation calculation of the energy of the ground state, the optimum screening constant S is such that the decrease in the estimate of the binding energy of the system, due to first-order terms in the interelectronic repulsion is $2A(Z-S)S$. (This latter term being the increase in binding energy associated with the increase of nuclear charge from the unperturbed $(Z-S)$ to the actual Z, treating this increase of nuclear charge as an infinitesimal.) But S so determined, is optimum for the estimation of the energy of the entire system; in a neon-like structure the $1s$ electrons will experience a field greater than that due to a nuclear charge $(Z-S)$, while the $2p$ electrons will be less tightly bound.

To obtain the S appropriate to the estimation of the ionization potential, the energies of the interactions of the six $2p$ electrons with the $1s$ and the $2s$ electrons and with one another are calculated; one-sixth of the sum gives an average energy of repulsion per $2p$ electron. S is so chosen that the perturbation of the nuclear charge increases the binding energy of each $2p$ electron to cancel exactly this average energy of repulsion, S again being treated as an infinitesimal. The fact that the field from a nuclear charge $(Z-S)$ fails to approximate closely that experienced by the $1s$ and $2s$ electrons is of minor consequence, since terms not involving the $2p$ electrons will not appear in the expression for the ionization energy.

S is chosen the same for the fluorine configuration as for the neon-like structure, then termwise subtraction of expressions of type (2) appropriate to the $1s^2 2s^2 2p^6$ and to the $1s^2 2s^2 2p^5$ configurations yields an estimate of the ionization energy $I(Z)$:

$$I(Z) \cong a(Z-S)^2 + b(Z-S) + c + d(Z-S)^{-1}. \quad (3)$$

Define

$$Q(Z) \equiv I(Z) - a(Z-S)^2 - b(Z-S)$$

and

$$Q'(Z) \equiv c + d(Z-S)^{-1}.$$

$I(Z)$ is known from spectroscopic data for systems isoelectronic with the ground state of neon for $Z \geq 10$; hence, $Q(Z)$ is known for $Z \geq 10$. The constants c and d are evaluated by setting $Q'(10) = Q(10)$ and $Q'(11) = Q(11)$. Using the values of c and d so determined, $Q'(12)$ and $Q'(13)$ are calculated; it is found that these approximate $Q(12)$ and $Q(13)$ so closely that one sets $Q'(9) \cong Q(9)$ with considerable confidence. The estimate of the electron affinity of fluorine is then determined from

$$I(9) \cong Q'(9) + a(9-S)^2 + b(9-S).$$

The spin-orbit interaction is excluded from the hamiltonian deliberately—for when this is present the contribution to the nth order of perturbation is no longer proportional to $(Z-S)^{2-n}$. To compensate for this omission the spectroscopic term values must be referred to the center of gravity of the multiplet, for purpose of determining $I(Z)$.

DETAILS OF CALCULATION

From the theory of the hydrogen atom it is evident that

$$a = 0.125000.$$

It is readily seen that b must satisfy

$$
\begin{aligned}
b(Z-S) = &-2J(2p, 1s) - 2J(2p, 2s) - 4J(2p_x, 2p_z) \\
&- J(2p_z, 2p_z) + K(2p, 1s) + K(2p, 2s) \\
&\qquad + 2K(2p_x, 2p_z) + S(2p_z/r^{-1}/2p_z),
\end{aligned}
$$

where $J(2p, 1s)$ denotes the direct integral $(2p, 1s/r_{ij}^{-1}/2p, 1s)$ and $K(2p, 1s)$ denotes the exchange integral $(2p, 1s/r_{ij}^{-1}/1s, 2p)$ etc. Substituting termwise, we have

$$
\begin{aligned}
b = &-2(0.242798) - 2(0.162109) - 4(0.174609) \\
&-0.195703 + 0.017070 + 0.029297 \\
&\qquad\qquad + 2(0.010547) + 0.250000S.
\end{aligned}
$$

Similarly, S is determined from

$$
\begin{aligned}
12J(2p, 1s) &+ 12J(2p, 2s) + 12J(2p_x, 2p_z) \\
&+ 3J(2p_z, 2p_z) - 6K(2p, 1s) - 6K(2p, 2s) \\
&\qquad - 6K(2p_x, 2p_z) - 6S(2p_z/r^{-1}/2p_z) = 0,
\end{aligned}
$$

i.e.,

$$
\begin{aligned}
12(0.242798) &+ 12(0.162109) + 12(0.174609) \\
&+ 3(0.195703) - 6(0.017070) - 6(0.029297) \\
&\qquad - 6(0.010547) - 1.500000S = 0.
\end{aligned}
$$

From these one finds

$$S = 4.799878,$$
$$b = -0.436522.$$

To convert from term values to the unit of energy herein employed one has only to divide the term value by twice the Rydberg constant appropriate to the system. The spectroscopic term values of the $1s^2 2s^2 2p^6$, $^1S_0$ state with respect to the $1s^2 2s^2 2p^5$, $^2P_{\frac{3}{2}}$ state for various Z values are tabulated in Table I; also tabulated is one third of the $1s^2 2s^2 2p^5(^2P_{\frac{3}{2}} - ^2P_{\frac{1}{2}})$ separation.[3] These must be added to give the term value from which $I(Z)$ is obtained.

By substituting for a, b, S, and $I(Z)$, the value of $Q(Z)$ is determined. Table II presents the details of the calculation; $Q'(Z)$ is identified with $Q(Z)$ at $Z=10$ and 11; $Q'(12)$ and $Q'(13)$ are included for comparison with $Q(12)$ and $Q(13)$. $Q(12)$ and $Q(13)$ straddle the $Q'(Z)$ line and the agreement is within the accuracy of the term values used to evaluate $Q(12)$ and $Q(13)$.

Estimating from column $(Z=9)$, $I(9) \cong 0.11679$. Converting this to wave numbers, and subtracting one third of the doublet separation in F spectrum, one obtains a term value corresponding to 72.86 kcal/g atom for the electron affinity of fluorine.

It is not a straightforward matter to assign a probable error to this estimate. It will be noted that, in estimating the electron affinity, relativistic effects have been ignored. The Thomas term has, of course, been taken into account in referring the term value to the center of gravity of the multiplet. The term in $\partial\phi/\partial r$ of the Dirac hamiltonian affects the energy levels of the s states only, for first-order perturbation of a coulomb potential. Consequently, the only neglected term is that corresponding to the relativistic mass correction. Inclusion of this term as a perturbation, increases the estimate of the affinity of fluorine by less than 1 kcal/g atom. If any systematic error is anticipated, surely this will be a tendency to overestimate the electron affinity, since the extrapolation formula is singular at $Z=4.799878$. The writer believes the electron affinity of fluorine to be 73 ± 3 kcal/g atom.[4]

THE INFERRED DISSOCIATION ENERGY OF FLUORINE

Mayer and Helmholz[5] have applied the Born-Haber cycle to the estimation of electron affinities of the halogens. They assert that their calculated values of

TABLE I. Spectroscopic data for the determination of $I(Z)$.

Z	$(^1S_0 - ^2P_{3/2})$ cm^{-1}	$\frac{1}{3}(^2P_{3/2} - ^2P_{1/2})$ cm^{-1}	$I(Z)$
9		135	
10	173930	261	0.793694
11	381528	455	1.740483
12	646364	742	2.948497
13	967783	1147	4.414860

TABLE II. Parameters in Eq. (3) for isoelectronic series.

	$Z=9$	$Z=10$	$Z=11$	$Z=12$	$Z=13$
$I(Z)$	?	0.79369	1.74048	2.94850	4.41486
$-a(Z-S)^2$	-2.20513	-3.38016	-4.80519	-6.48022	-8.40525
$-b(Z-S)$	1.83345	2.26997	2.70649	3.14301	3.57953
$Q(Z)$	?	-0.31650	-0.35822	-0.38871	-0.41086
$Q'(Z)*$	-0.25489	-0.31650	-0.35822	-0.38838	-0.41117

* $c = -0.57527$; $d = 1.34563$.

lattice energies are reliable to ±3 kcal/mole; since the principal source of error in the thermochemical cycle lies in the lattice energy this is probably the error that should be assigned to the cycle. The excellent agreement between the directly measured affinities of chlorine,[6] bromine,[7] and iodine[8] and the estimates by Mayer and Helmholz suggest that this is indeed the case.

Accepting this accuracy, and assuming the electron affinity of fluorine to be 73 ± 3 kcal/g atom, the inferred dissociation energy of fluorine would be about 18 ± 12 kcal/mole.

An excellent review of the existing state of confusion on the thermochemistry of fluorine and related compounds as they affect the estimation of the dissociation energy of fluorine is due to Evans et al.[9] They conclude "that the experimental data at present available as a whole indicate strongly a value for $D(F_2)$ of about 37 kcals g mole^{-1}, certainly not greater than about 45 kcals g mole^{-1}." Their recommendation of 37 ± 8 kcal/mole is barely compatible with the estimate of this paper.

More recently Schumacher[10] has reported that, on the assumption that the complete dissociation of fluorine oxide requires approximately twice the energy of dissociation of one fluorine atom, the energy for complete dissociation of fluorine oxide is 81 ± 6 kcal/mole. The heat of formation of fluorine oxide he gives as -7 ± 2 kcal/mole. The inferred dissociation energy of fluorine is 30 ± 8 kcal/mole.

Note added in proof:—In a letter to this Journal (J. Chem. Phys. 19, 1070 (1951), Doescher reports an experimental determination of the heat of dissociation of fluorine. His results indicate that the error in the calculated lattice energy for alkali fluorides together with the error in the writer's estimate of the electron affinity of fluorine must be about 10 kcal/mole rather than 6 kcal/mole as the writer had estimated.

[3] Taken from R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), and from *Annual Tables of Physical Constants and Numerical Data* (Frick Chemical Laboratory, Princeton, New Jersey, 1942). This latter source contains a typographical error in that the term values for Na II are stated to be with respect to $^2P_{\frac{3}{2}}$ state of Na III, while in fact they are referred to the $^2P_{\frac{1}{2}}$ ground state of Na III, as is apparent from a paper by J. E. Mack and R. A. Sawyer, Phys. Rev. **35**, 299 (1930).

[4] Discussed more fully in writer's dissertation, "On the Electron Affinity of Fluorine—an Estimate of the Electron Affinity with a Discussion of the Inferred Dissociation Energy," Stanford University, 1951.

[5] J. E. Mayer and L. Helmholz, Z. Physik. **75**, 19 (1932).

[6] McCallum and Mayer, J. Chem. Phys. **11**, 56 (1943).

[7] Weissblatt, dissertation, The Johns Hopkins University, Baltimore, Maryland, 1938.

[8] Sutton and Mayer, J. Chem. Phys. **3**, 20 (1935).

[9] Evans, Warhurst, and Whittle, J. Chem. Soc., 1524 (June 1950).

[10] H. J. Schumacher, Chem. Abstracts **45**, 2300^b (1951).