

appears to satisfy the requirements for a Cole-Cole representation. The dielectric loss at frequencies 6, 15, and 24 kMc indicates that any changes in the dielectric loss for a random orientation are very small as anisaldazine passes from its anisotropic to normal liquid phase. This implies that the anisotropic phase of anisaldazine

might satisfy the requirements for a Cole-Cole representation reasonably well.

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## Absorption Spectrum of Gaseous $F^-$ and Electron Affinities of the Halogen Atoms

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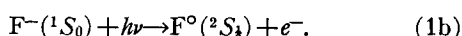
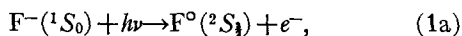
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The absorption spectrum of gaseous fluoride ion has been observed in shock-heated vapors of CsF, RbF, and KF. The spectrum is a continuum with two sharp thresholds at 3595 and 3542 Å, similar to those of the other halide ions. The electron affinity determined from the low-energy threshold is  $3.448 \pm 0.005$  eV. The cross-section for photodetachment at 3565 Å is about  $2.5 \pm 2 \times 10^{-18}$  cm<sup>2</sup> and at 3525, about  $3.3 \pm 2 \times 10^{-18}$  cm<sup>2</sup>. The electron affinities of chlorine, bromine and iodine are revised, respectively, to 3.613, 3.363, and 3.063 eV, all with uncertainties of 0.003 eV.

THE electronic absorption spectra of hot vapors of alkali halides have been a subject of recent study.<sup>1,2</sup> The concentrations of the free gaseous ions  $Cl^-$ ,  $Br^-$ , and  $I^-$  proved large enough that absorption spectra of these species could be observed. Moreover the spectra, which are continua with sharp low-energy thresholds, provided quite precise values of the electron affinities of Cl, Br, and I. Unfortunately, an unambiguous identification of the fluoride spectrum could not be made from results obtained under those conditions which yielded the spectra of the other ions.

The technique developed previously has now been used to obtain the absorption spectrum of  $F^-$  in the region of its photodetachment thresholds. Fluoride salts of cesium, rubidium, and potassium have been vaporized and dissociated in a shock tube, and a flash lamp triggered by the shock wave has served as the source for absorption spectra. Two sharp changes in extinction have been found which are similar to those reported for the other halides. These are assigned, on the basis of their separation and relative intensities, to the onsets of the photodetachment processes



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<sup>1</sup> R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.* **35**, 2237 (1961).

<sup>2</sup> R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.* **37**, 2278 (1962).

Ion densities estimated from alkali atom linewidths determine the photodetachment cross-section of an absorbing fluoride ion.

The apparatus was described in detail previously.<sup>2</sup> Spectra were all taken with a Bausch & Lomb medium quartz spectrograph, on Eastman 103-0 plates. Figure 1 is a reproduction of that portion of a typical spectrogram which shows the two thresholds of  $F^-$ . As in the previous work, threshold wavelengths estimated visually were systematically lower than the value determined photometrically. The differences for fluoride were 8–10 Å, somewhat greater than for the heavier ions. This seems to be associated with the fact that the  $F^-$  extinction curve appears to rise more gradually than do the continua of  $Cl^-$ ,  $Br^-$ , and  $I^-$ . The threshold wavelengths of fluoride ion could not be determined with quite as much precision as those of the other halides, both because of the lower slope and because of interfering weak absorption lines of iron. These become troublesome only with the relatively strong shocks required to generate  $F^-$ .

The only differences from previous experiments were the somewhat stronger shocks necessary to vaporize and dissociate the fluoride salts. The heats of vaporization of KF, RbF, and CsF are 41.27, 39.51, and 34.33 kcal/mole, fairly similar to 34.69, 35.96, and 35.93 kcal/mole for the iodides of the same alkalis.<sup>3</sup> However, the dissociation energies (to atoms) of the diatomic

<sup>3</sup> L. Brewer, "The Fusion and Vaporization Data of the Halides" in *The Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics*, edited by L. L. Quill (McGraw-Hill Book Company, Inc., New York, 1950).

KF

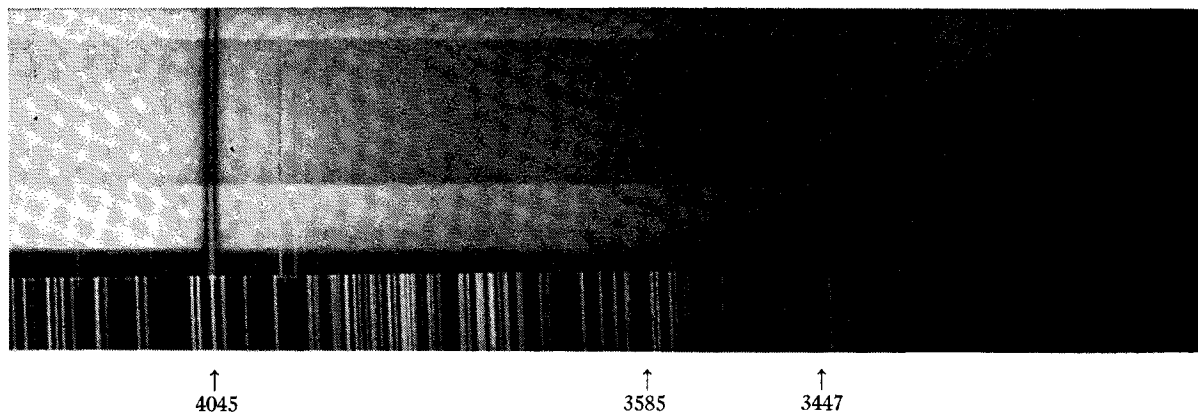


FIG. 1. Typical spectrogram showing the long-wavelength threshold of the photodetachment continuum of  $F^-$ . The second threshold is barely visible to the eye on the original plate. Potassium fluoride is the shocked salt; driving gas was  $H_2$  at 410 psi; driven gas was Ar at 1.8 cm Hg. The indicated wavelengths 4045 and 3447 Å are those of the  $5p$  and  $6p$  lines of potassium. The lower-energy threshold of  $F^-$  appears to the eye to lie at 3585 Å, but, as discussed in the text, microdensitometer tracings show that this is approximately the shoulder of extinction rather than the toe.

fluorides of potassium, rubidium, and cesium are 117.6, 116.1, and 119.6 kcal/mole compared with the iodide dissociation energies of 76.8, 76.7, and 82.4 kcal/mole.<sup>4</sup> The dissociation energies of the fluorides, especially, make detectable concentrations of  $F^-$  hard to produce by comparison with the other halides. This is because these energies make the dissociation constants of the fluorides smaller than the other alkali halide dissociation constants by a factor of 10 or more at 4000°K and at least a hundred-fold smaller than the other constants at 3000°K.

It proved desirable to use KF as a source of fluoride ion despite its unfavorable thermodynamics because of the problem of interference by atomic lines of rubidium and cesium. The cesium  $9p$  lines fall at 3612 and 3617 Å, and the rubidium  $7p$  lines, at 3587 and 3592 Å; potassium has no absorption lines in this region.

The thresholds we have observed and attributed to  $F^-$  fall at  $3595 \pm 5$  Å and at  $3542 \pm 2$  Å. The long-wavelength threshold can be located most precisely with KF as the source, and can be identified in vapor of CsF. Small quantities of Rb, however, make it impossible to locate this threshold, and the iron lines in this region mentioned above also add a bit to the uncertainty. The short wavelength transition to  $F(^2P_{3/2}) + e^-$  can be seen with KF but can be located most precisely with the more efficient source CsF. The curve of relative cross section vs wavelength for a typical plate is shown in Fig. 2. As in the case of the heavier halides, the steps are relatively sharp, consistent with the threshold law  $\sigma \propto (E - E_0)^{3/2}$  expected for the 1-electron transition from a bound  $p$ -level to an  $s$ -state in the continuum.<sup>5</sup>

The threshold energies are  $3.447 \pm 0.005$  and  $3.499 \pm 0.001$  eV, and have a separation of  $416 \pm 43$   $cm^{-1}$ . This must be compared with the doublet separation of 404  $cm^{-1}$  in the fluorine atom.<sup>6</sup> The threshold relative intensities are consistent with the 2:1 intensity ratio expected with simple  $L-S$  coupling. The uncertainties in intensities are rather large, so that no quantitative claims can be made for agreement with this ratio, beyond the discussion given below.

The experimental extinction curve can be compared with the calculated curve of Cooper and Martin. A detailed quantitative comparison of calculated and observed photodetachment cross-sections cannot yet be made because the experimental measurements extend only about 0.1 eV above the threshold, and the first computed point falls 0.25 eV above the threshold. Nevertheless, some qualitative information can be inferred at this stage.

The calculated curve for  $F^-$  appears to rise more slowly than does the experimental curve, which as Fig. 2 shows, is quite steplike. The theoretical and experimental photodetachment cross sections of  $Cl^-$  also differed in that the calculated function did not rise and flatten as the experimental curve did, but rose to a peak more than 10 eV beyond the threshold. In this sense, the agreement of calculation and experiment is not so good for  $F^-$  and  $Cl^-$  as it was in the cases of  $C^-$  and  $O^-$ .<sup>7-9</sup> On the other hand, the calculated cross-sections of  $F^-$  and  $Cl^-$  were based on Hartree wavefunctions of the neutral atoms, rather than on Hartree-Fock

<sup>6</sup> C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circ. No. 467, Vol. I (1949).

<sup>7</sup> J. W. Cooper and J. B. Martin, Phys. Rev. **126**, 1482 (1962).

<sup>8</sup> M. Serman and L. M. Branscomb, Phys. Rev. **125**, 1602 (1962).

<sup>9</sup> L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

<sup>4</sup> L. Brewer and E. Brackett, Chem. Rev. **61**, 425 (1961).

<sup>5</sup> E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

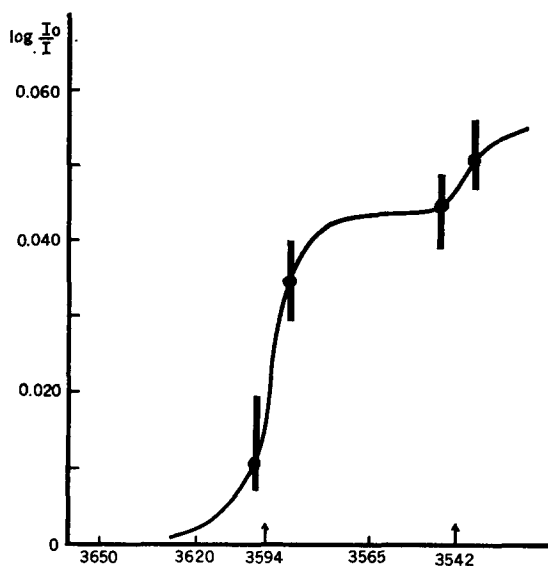


FIG. 2. Extinction curve of  $F^-$  taken from a typical spectrogram, showing representative points and uncertainties. Shocked salt, KF; driving gas,  $H_2$  at 400 psi; driven gas, Ar at 2 cm Hg.

functions. The latter were used for the oxygen and carbon calculations. These two functions differ considerably in their outer parts, and as Cooper and Martin point out, the cross section for photodetachment is rather sensitive to the wavefunction far from the nucleus. A more nearly accurate calculation could presumably be done if the potential of the Hartree-Fock distribution were used to represent the unpolarized core.

The magnitude of the photodetachment cross section derived by Cooper and Martin seems to be in reasonably good agreement with the experimental value found in this work. Total ion concentrations are estimated from atomic linewidths, as described previously,<sup>1,2</sup> and at the temperatures of the salt vapors ( $\sim 3000^\circ\text{--}3500^\circ\text{K}$ ), the negative halide ion concentrations can be taken as half the total, since electron concentrations are very small. The ion density measurements seem to be more reproducible and precise than the extinction due to the negative ions. This raises some question about the validity of the assumption of thermal equilibrium among possible associated species, and in particular of the possibility of the presence of neutral atoms or molecules associated with negative ions. The problem of thermal equilibrium is under investigation at the present time. In any event, negative ion concentrations in the shocks used for estimating the cross-section of  $F^-$  were between  $0.5$  and  $1 \times 10^{15} \text{ cm}^{-3}$ . The experimental cross-sections for the processes  $F^-(^1S_0) \rightarrow F^0(^2P_{3/2})$  and  $F^-(^1S_0) \rightarrow F^0(^2P_{1/2})$  are, respectively,  $2.5 \pm 2 \times 10^{-18} \text{ cm}^2$  and  $0.8 \pm 0.4 \times 10^{-18} \text{ cm}^2$ , at wavelengths  $20 \text{ \AA}$  above the corresponding thresholds. The curves at these points are reasonably flat. The total experi-

mental cross-section of  $\sim 3.3 \times 10^{-18} \text{ cm}^2$  at an energy of  $0.07 \text{ eV}$  above the low-energy threshold is in reasonable agreement with the calculated value of  $4.0 \times 10^{-18} \text{ cm}^2$  at an energy  $0.25 \text{ eV}$  above the threshold. The experimental and computed points certainly can lie on a simple curve. Moreover, the computed cross-section for  $F^-$  is about one-third to one-fifth the  $Cl^-$  cross section, which is very much in accord with the results of the experiments described here and previously.<sup>2</sup>

We can make a comparison between the electron affinity of fluorine derived from this work and values obtained by other methods. The *a priori* theoretical value<sup>10</sup> of  $1.39 \text{ eV}$  is quite far from the experimental values but is of the correct sign. Semiempirical extrapolations have given values of  $3.50$ ,<sup>11</sup>  $3.47$ ,<sup>12</sup> and  $3.34 \text{ eV}$ .<sup>13</sup> Some experimental values obtained recently are  $3.62 \pm 0.09 \text{ eV}$ , from surface ionization measurements of Bailey,<sup>14</sup>  $3.45 \text{ eV}$  from lattice energy calculations,<sup>15</sup> and  $3.33 \text{ eV}$  from the surface ionization measurements of Bakulina and Ionov.<sup>16</sup> (The last is based on a value of  $3.36 \text{ eV}$  for Br, rather than the  $3.50 \text{ eV}$  value assumed by Bakulina and Ionov.) The conclusion of the work reported here is a value of  $3.448 \pm 0.005 \text{ eV}$  for the electron affinity of fluorine.

The affinity of fluorine just quoted,  $3.448 \text{ eV}$ , does not include the "correction" due to the potential of mean force of the ion atmosphere which was discussed in earlier work<sup>1,2</sup> and which was added to the observed threshold energies to give the values reported for the halogen electron affinities. (The Debye-Hückel potential for the fluoride spectra would, incidentally, be  $0.012 \pm 0.003 \text{ eV}$ .) Reconsideration of the effect of the Debye-Hückel potential indicates clearly that introduction of the potential was an incorrect procedure. The electron undergoing photodetachment moves from a bound state to a continuum state in a potential which is the sum of the atomic potential and the potential of the ion atmosphere. The latter is essentially a constant,  $-eR$ , so that the solutions of the Schrödinger equation are all shifted downward by this same constant amount. Consequently, the separation of the bound state and the continuum is unaffected by the Debye-Hückel potential itself, so that no correction is warranted. However, on a more refined level the fluctuations of the ionic atmosphere produce a fluctuating and nonuniform potential, which in turn introduces Stark shifts and Stark broadening characteristic of the individual levels. The fluctuations will therefore introduce a lowering of the energy of the photodetachment threshold, since the continuum limit is presumably

<sup>10</sup> L. C. Allen, *J. Chem. Phys.* **34**, 1156 (1961).

<sup>11</sup> B. Edlen, *J. Chem. Phys.* **33**, 98 (1960).

<sup>12</sup> J. W. Edie and F. Rohrlach, *J. Chem. Phys.* **36**, 623 (1962).

<sup>13</sup> C. W. Scherr, J. N. Silverman, and F. A. Matsen, *Phys. Rev.* **127**, 830 (1962).

<sup>14</sup> T. L. Bailey, *J. Chem. Phys.* **28**, 792 (1958).

<sup>15</sup> D. Cubicciotti, *J. Chem. Phys.* **34**, 2189 (1961).

<sup>16</sup> I. N. Bakulina and N. I. Ionov, *Dokl. Akad. Nauk S.S.S.R.* **105**, 680 (1955).

shifted more to lower energies than is a bound ground state. The actual magnitude of the Stark shifts must be small; the shifts of atomic lines of the alkalis are less than 1 Å in the spectra we have observed, and the fluctuations in the electric field about an ion are expected to be much less than those about an atom.<sup>17</sup> Consequently, we can expect the observed threshold energies to deviate from the actual electron affinities, but only very slightly and perhaps not observably. Broadening of the threshold is expected to be a much larger effect than shifting, if the foregoing argument is correct. This is in fact what we have observed; the shapes of the toes of the absorption curves are much more sensitive to shock conditions than are the actual positions of the curves as measured by their points of inflection or extrapolated threshold positions.

We have collected in Table I the electron affinities of the four halogens derived from absorption spectra of the halide ions. It should be noted that without the Debye-Hückel potential, the iodine affinity derived from absorption spectroscopy is 0.013 eV lower than the photodetachment value of 3.076 eV of Steiner, Seman, and Branscomb.<sup>18</sup> The photodetachment value is, however, based on the assumption that the extinction curve can be represented very well by a step function. Any finite curvature in the extinction must result in a lower value for the affinity derived by the photodetachment method. The value 3.076 eV therefore represents an upper limit, strictly, for the electron affinity of iodine.

Table I includes, in addition to the electron affinities, the average energies of the halogen  $^2P$  terms relative

TABLE I. Electron affinities of the halogens from absorption spectra.

| Element | Electron affinity (eV) | Statistically weighted average energy difference of neutral atom ( $^2P$ ) and negative ion ( $^1S$ ) |
|---------|------------------------|---|
| F       | 3.448±0.005            | 3.464   |
| Cl      | 3.613±0.003            | 3.649   |
| Br      | 3.363±0.003            | 3.515   |
| I       | 3.063±0.003            | 3.377   |

to the halide ion energies. These represent the energy differences between the lowest electronic configurations of the halogen atoms and negative ions. There can be no more doubt that chlorine has the largest electron affinity of all atoms. Moreover, the "configuration electron affinity," as this quantity might be called, is larger for bromine than for fluorine. The consideration of average energies was suggested by Roothaan,<sup>19</sup> in order to avoid confusion between atomic spin-orbit coupling and effects within the negative ion. It is clear from the table that the energy difference of the closed-shell  $s^2p^6$  configuration is still greatest for chlorine, but that all the halogens are somewhat more alike than the affinities alone would indicate.

#### ACKNOWLEDGMENT

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<sup>17</sup> B. Moser and M. Baranger, Phys. Rev. **118**, 626 (1960).

<sup>18</sup> B. W. Steiner, M. L. Seman, and L. M. Branscomb, J. Chem. Phys. **37**, 1200 (1962).

<sup>19</sup> C. C. J. Roothaan (private communication).