If there is a decrease in the translational symmetry of the crystal, with respect to exciton migration, then the energy becomes localized, or "trapped," on this defect for a longer period of time than the normal residence time (the question of the meaning of residence time is open for discussion but is not pursued here). If the defect is a bond or molecule, than the energy localized on the defect has a greater probability of degrading by bond dissociation than it would if it had remained localized. In the case of D₂O containing small amounts of H₂O, which should more properly be considered as a mixture of HOD in D₂O, the zero-order wavefunction is composed principally of O-D vibrations. Therefore, the occasional O-H bond with its considerably different vibrational motion may act as a relatively effective trap for the electronic excitation, thus causing the O-H bond rupture to occur more readily. In this manner, the main D₂O matrix acts as an energy-transfer medium carrying energy from the ionizing radiation to the O-H bonds, which would therefore dissociate with a much greater rate than would be predicted on the basis of the number of OH bonds present. As the concentration of H₂O goes up, the zero-order wave functions must contain the O-H vibrations as well as the O-D vibrations. Consequently, the unique efficiency of the O-H bonds as traps decreases, and no isotope effect is observed. Possible reasons for our failure to observe a corresponding abnormally high yield of D in H₂O due to the natural abundance of the heavy isotope, are discussed in the experimental section of this paper.²

As a final point, it should be mentioned that the microwave power saturation behavior of the H atoms formed from trace amounts of H₂O in D₂O was considerably different from that of atoms formed in all the other experiments. A power saturation study on the spectra showed that H and D have very similar relaxation times either in pure H₂O or D₂O, respectively, or in the mixed solutions. However, the H atoms exhibiting the strong isotope effect in the trace system discussed above were very much more susceptible to power saturation than were the other trapped atoms. The magnitude of the difference in ease of saturation indicates that the relaxation times differ by more than an order of magnitude. An important difference in the trace H₂O in D₂O samples over the other mixed samples is that the H atoms are completely surrounded by D nuclei in the former case and by both H and D nuclei in the latter case. This suggests that the main relaxation path to the lattice is via the nuclear dipole interactions and that H interacts more effectively with other H nuclei than with D nuclei and vice versa.

An obvious approach toward resolving this question would be a series of experiments with various small concentrations (e.g., 0.1% to 5%) of H₂O in D₂O and vice versa. Such experiments should at least reveal the maximum concentration of "impurity" water at which preferential exciton decay occurs to a significant extent, and if this level is sufficiently high (i.e., >0.1%), then the symmetrical isotope effect for D in nearly pure H₂O should be observed. Unfortunately, further experiments along this line were prevented by the expiration of the research contract.

Absorption Spectra of Gaseous Halide Ions and Halogen Electron Affinities: Chlorine, Bromine, and Iodine

R. Stephen Berry, Curt W. Reimann, and G. Neil Spokes
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut
(Received June 18, 1962)

Absorption spectra have been taken of partially dissociated vapors of chloride, bromide, and iodide salts of rubidium and cesium. The salts have been heated by shock waves. Continuous absorption spectra characterized by sharp thresholds are attributed to the ions Cl⁻, Br⁻, and I⁻. The low-energy thresholds for the three ions fall at approximately 3424, 3685, and 4040 Å, respectively. From the threshold wavelengths and appropriate small environmental corrections, the electron affinities of chlorine, bromine, and iodine are determined to be 3.628±0.005, 3.378±0.005, and 3.078±0.005 eV, respectively.

I. INTRODUCTION

SPECTRA of negative atomic ions have been observed under a variety of conditions and with a variety of techniques. Absorption spectra have been reported for several ions in solution.²⁻⁴ The absorption due to H²⁺ is observable in the spectrum of the limb of the sun.⁵ Laboratory measurements of photodetachment of gaseous negative ions have been made by a crossed ion–photon beam technique.⁶ Emission spectra of gaseous negative ions have been observed in arcs⁷⁻⁹ and behind shock fronts.¹⁰⁻¹¹

¹ Present address: Stanford Research Institute, Menlo Park, California.
³ G. Scheibe, Ber. 99, 1323 (1926).
In this discussion, we present the observations and conclusions based on a technique somewhat different from any of the afore-mentioned. We have made direct photographic measurements of continuous absorption spectra which we attribute to the free gaseous ions Cl⁻, Br⁻, and I⁻. These have been detected in the vapors of the corresponding rubidium and cesium salts produced by shock heating. A preliminary report of the spectrum of Cl⁻ has already been made.12

The application of shock-wave spectroscopy to the problem of negative ions is attractive insofar as it may permit us to determine quantities or observe species which are inaccessible or less precisely measurable by other techniques. For example, the resolution of the photographic method may allow one to measure the shape of a continuous absorption curve, and to see bumps and inflections which would only be observed with great difficulty, if at all, with other methods. Moreover, one has the opportunity to study the interactions of ions with other species, albeit not in quite the detail that a colliding beam system might afford. These interactions do draw attention to one of the potential limitations of the method we have used; namely, that the interactions will always influence the observable spectra and so must be taken into account when the spectra are interpreted.

That the method is practicable can be seen by the following argument. Let us consider cesium iodide, as a typical salt. Its dissociation energy is 3.4 eV,13 the ionization potential of Cs is 3.893 eV,14 and we may take the electron affinity of I as about 3.1 eV (see below). The moment of inertia is 713.67 amu·Å²,15 and the vibrational frequency is about 101 cm⁻¹.16 The equilibrium constant for the gas-phase reaction

\[ \text{CsI} \rightleftharpoons \text{Cs}^+ + \text{I}^- \]

at any desired temperature can be calculated readily from these data. We write the equilibrium constant as a product of factors \( f_{\text{tr}}, f_{\text{rot}}, f_{\text{vib}}, \) and \( f_{\text{e}} \) for translational, rotational, vibrational, and electronic degrees of freedom. We neglect the correction to \( f_{\text{e}} \) for gas imperfections since it is small (<5%) for the work described below. Then if \( n(X) \) is the number density for species \( X \), in cm⁻³, we have

\[
K = n(\text{Cs}^+)n(\text{I}^-)/n(\text{CsI}) = f_{\text{tr}}f_{\text{rot}}f_{\text{vib}}/f_{\text{e}}
\]

\[
= (5 \times 10^6) \times (10^{-5}) \times (5 \times 10^{-2}) \times (2 \times 10^{-8})
\]

\[= 5 \times 10^{17} \text{ at } 3000^\circ K.\]

\[K = (10^8) \times (8 \times 10^{-4}) \times (1.6 \times 10^{-2}) \times (2 \times 10^{-6}),\]

\[= 2.6 \times 10^{19} \text{ at } 4000^\circ K.\]

Comparison of these numbers shows clearly that the translational entropy of dissociation and the rapidly increasing exponential containing the heat of reaction together lead to an equilibrium in which the ion densities may be sizeable. The relative population of dissociated atoms is easily determined; the relevant factors are again the ionization potential of Cs and the electron affinity of I, and the fine-structure splitting of the \( ^2P_1 \) and \( ^2P_3 \) states of the iodine atom, 7603 cm⁻¹.14 From the data, we find that the ratio \( n(\text{Cs}^+)n(\text{I}^-)/n(\text{CsI}) \) is approximately 170 at 3000° and 80 at 4000°. If we neglect the possible presence of free electrons and I₂ molecules for the moment, we can set \( n(\text{Cs}^+) = n(\text{I}^-) \) and \( n(\text{Cs}^+) = n(\text{I}^-) \), and conclude that the ratios \( n(\text{Cs}^+)/n(\text{I}^-) \) are about 13 and 9 at 3000° and 4000°K, respectively. The presence of free electrons can influence this ratio considerably at temperatures of 4000° or higher, when the equilibrium constant

\[ n(e^-)n(\text{I}^-)/n(\text{I}_2) \]

becomes \( 3.4 \times 10^{17} \) cm⁻³. Since the dissociation constant \( n(\text{I}_2)/n(\text{I}^-) \) is \( 3.6 \times 10^{22} \) cm⁻³ at 4000°K, the I₂ concentration is essentially zero. From these figures, we conclude that total salt concentrations of about \( 10^{17} \) cm⁻³ at temperatures between 3000° and 4000°K lead to free iodide concentrations of \( 10^{15} \) to \( 5 \times 10^{14} \) ions/cm³.

If thermal equilibrium were not achieved, presumably the electron concentration would be lower than the equilibrium value and the negative ion concentration, correspondingly larger. If atom-ion equilibrium were not achieved, one would again expect the negative-ion concentration to exceed the equilibrium value, because if the vaporization process were too rapid to yield an equilibrium mixture of atoms and ions, it would produce an excess of dissociated ion pairs as the result of the diabatic dissociation.17 The occurrence of either of these processes would not be surprising, particularly if the sample could be observed very quickly after heating. Delays in the onset ionization have been observed in shock waves,18,19 and overabundances of ions have been observed in flames containing alkali salts.20

One must ask next whether free negative ion concentrations of about \( 10^{16} \) to \( 5 \times 10^{15} \) ions/cm³ may be detectable spectroscopically. The halide ions would be expected to show continuous absorption as they undergo photodetachment

\[ X^- + hv \rightarrow X^2 + e^- \]

(1)

Cross sections for this process have been determined for several species. We may assume from these results that for such a cross section \( \sigma = 10^{-19} \) cm\(^2\) is a reasonable estimate. Therefore, with an optical path of 20 cm or more, it should be possible to detect the absorption spectra of the free halide ions.

The shock tube becomes a particularly appealing device for heating salts when one realizes the temperatures and optical paths required for the experiments. In fact, emission studies of vapors of shock-heated salts have been made, and alkali salts in particular have been introduced in order to study atomic line reversal. The extension of well-known techniques of flash-absorption spectroscopy to the study of salt vapors appears therefore as a simple and logical technique.

In the sections following, we describe the apparatus and experimental procedure, the experimental results, and the interpretation of these results in terms of the behavior and properties of the shocked salts, and in particular, of the negative ions.

II. EXPERIMENTAL

A. Apparatus

The apparatus has been described briefly. A slightly more detailed description is given here. It is shown schematically in Fig. 1.

The shock tube is steel, with an interior cross section 8.5 x 8.5 cm. The driver section is 5 ft long; the low-pressure section consists of five 3-ft sections which can be taken apart rather conveniently. At the time the work described below was carried out, one section was equipped with three resistance gauges, made of platinum (Hanovia) painted in thin strips on glass rod. These were essentially the same as the gauges described by Clouston, Gaydon, and Hurle. Another section was equipped with clear fused-silica windows on opposite sides of the tube, and on the top as well. A small aluminum beam could be mounted on the tube; this beam carried the three front-surfaced mirrors of a multiple-reflection system. The mirrors were made from lens elements supplied by the Argus Camera Corporation.

The shock was initiated by spontaneous bursting of a scribed aluminum diaphragm. Diaphragms 0.063 in. thick with scribed crosses 0.019 in. deep burst at about 300 \( \pm \) 10 psi; diaphragms 0.080 in. thick and scribed to a depth of 0.030 in. burst at about 350 \( \pm \) 10 psi. Most experiments were carried out with driver gas \((H_2)\) pressures between 200 and 400 psi. At pressures above about 325 psi, the thermal gauges became unreliable, and sometimes were partially stripped away.

The low-pressure gas was generally commercial argon, used without purification, at pressures between 1.5 and 2.5 cm Hg. Krypton has been tried also, in the examination of very strong shocks.

Passage and velocity of the shock were determined with the use of the resistance gauges. Each gauge had a resistance of about 500 \( \Omega \) and was part of a simple battery-fed bridge. A voltage change from each was amplified and converted to a pulse which was displayed on the screen of an oscilloscope (Tektronix 533), which was itself triggered by the first arriving signal. The oscilloscope also supplied a gate signal to a variable delay circuit. The output of the delay was used as the trigger signal for the flash-absorption lamp circuit. A crowbar tube (KU 402) was used to discharge a capacitor bank (of 3.3 mF charged to 11 kV) through the fused-silica capillary lamp. The lamp itself was operated at a pressure slightly less than 1 mm Hg; the gas was air, pumped continuously. The lamp intensity fell to about 10% of its peak value in 20-25 \( \mu \)sec.

Most of the spectroscopic work was carried out with a Bausch & Lomb medium quartz spectrograph and Kodak 103-0 plates. Some work was also done with a small Hilger I/4 instrument and with a Hilger long-wave, glass-prism spectrograph, E414.

Plates were developed at 68°-70°F in D-11 or D-19 developer for 5 min.

Determinations of cross sections required plate calibrations, which were obtained with the use of a factory-calibrated seven-step neutral density filter. It was found that calibration of individual plates was not necessary; the uncertainties due to differences in plate response were considerably smaller than uncertainties arising from determinations of ion concentrations, for example, or of temperatures.

Plates were traced on a Leeds and Northrop Knorr-Albers recording microdensitometer, whose response was checked against the calibration of the neutral-
density step filter. Agreement within about 2% was found for the various optical densities. Wavelength measurements were made both from tracings and from direct measurement with a traveling microscope. Iron arc lines and convenient internal standards were used.

Salts used were generally the purest available materials, 99.5 to 99.9% pure, and were used without further purification. They were obtained from BDH and A. D. MacKay. Salt samples were introduced into the shock tube at a point 90 cm upstream from the observation windows. The salts were deposited on strips of cleansing tissue or thin, perforated aluminum foil. The strips were a little longer than the inside dimension of the tube and could be clamped easily between the flanges of adjoining sections of the tube.

B. Procedure

The normal operating procedure was this. The salt was deposited on the supporting material and dried in air, under an infrared heat lamp. The sample was put in place in the shock tube, the aluminum diaphragm was inserted, and the tube was evacuated to a pressure less than 50 μ, often to 15 μ or less. The high-pressure chamber was evacuated and then filled with hydrogen, to about 50 psi. The low-pressure section was pumped while the final optical alignment was carried out and a comparison spectrum was taken. Then the system was closed, inert gas was admitted to the low-pressure section, the spectrograph and electronics were set for operation and hydrogen was admitted to the high-pressure section until the diaphragm burst. The time during which the low-pressure system stood closed at a pressure below atmospheric was usually about 5 min and rarely exceeded 10 min. The leak rate of the shock tube was about 1 μ/min, so that no more than 0.1% of air contaminant was admitted during the standing period. Occasionally, comparison spectra were taken of shocks through supporting material alone. These were often included on plates with spectra of shocked salts. Except for lines and bands which could be attributed unambiguously to the supporting material, these comparison spectra were indistinguishable from other comparison spectra taken through the same optical system but without any shock.

For most work, plates were developed immediately after the last exposure was made. However, several plates, especially some of those intended for photometry, were left undeveloped for a time at least equal to the interval between the first and last exposure. No significant differences were found between these and other plates.

Plates were washed, after fixing, in tap water, wiped
gently to remove the surface deposit from the tap water, washed in distilled water, and air dried.

III. EXPERIMENTAL RESULTS

Typical absorption spectra of the heated salt vapors behind shocks are shown in Figs. 2, 3, and 4. The most obvious features are, of course, the principal series lines of the neutral alkali atoms. The forbidden \( 6d \rightarrow n' \) series are also easily recognized; \( 6d \) falls at a frequency slightly higher than \((n+1)p\). Figure 5 shows contours of two typical lines. The forbidden lines of the \( 5\rightarrow 3 \) series can also be identified, but these are quite weak, particularly for low \( n \). We have also observed a number of absorption lines arising from excited-excited transitions. For example, the \( 5f \rightarrow 5d \), \( 9p \rightarrow 5d \), \( 6d \rightarrow 6p \), \( 8s \rightarrow 6p \), and \( 9s \rightarrow 6p \) transition of cesium have all been identified.

Other atomic lines, not due to alkalis, have also been identified. Aluminum lines at 3082 and 3092 Å, and 3944 and 3961 Å appear in emission when aluminum inserts or electrodes are used in the flash lamp. The same lines appear also in absorption when aluminum is used as a supporting material for the salts. Sodium, calcium, iron, and copper are always detectable. Iron lines are especially intense when driving pressures over 350 psi are used.

The only molecular band systems identified positively in these experiments are the ubiquitous OH and \( \text{C}_2 \) (Swan) systems. Both appear when cleansing tissue is used as a supporting material. The 2-0, 1-0, and 0-0 bands of \( \text{C}_2 \) have been observed. The OH system can be detected if the salt is incompletely dried.

The most noteworthy features of the spectra are not the lines or bands, but the continuous absorption. The continua are unlike those associated with atomic ionization or normal molecular dissociation or even with alkali halide dissociation, the “fluctuation bands.”

The continua which we observe are characterized by a very sharp onset of extinction with increasing frequency. The absorptions rise from zero to relatively large values in intervals of only a few angstrom units. In all cases the curves of extinction show negative curvature and positive or zero slope over the entire ranges which we have observed, except for small tocs at the thresholds. In many cases the absorption curves are approximately horizontal for rather long intervals, so that the curves show two such steps very clearly. It is usually somewhat easier to see one step than the other on any given plate, simply because the plate

---

density varies too much to keep both steps in the convenient range of gray. The lower-energy step corresponds to a larger extinction than the high-energy step, so it is usually easier to detect visually.

The continua have the following characteristics. Their appearances are independent of alkali metal but are uniquely associated with the halogen present. The intensities of the continua increase from zero when driving pressures are about 200 psi, to essentially complete absorption beyond the long-wavelength threshold, when driving pressures are as high as 350 psi. Intensities depend also on sample size and are reasonably well correlated with both the intensity and width of the alkali atomic lines. These all imply that the absorbers are atomic species, presumably halogens, coming from the salts.

The identification of the species is now relatively simple. Neutral halogen molecules are present in quantities too small to be detected; this was indicated in the introduction. Ionized halogen molecules are ruled out on the same grounds. The alkali halide spectra are known and are quite different from the observed continua. Neutral atomic halogen absorbers can be excluded on the basis that their known absorption falls in the vacuum ultraviolet region, and the temperatures (surely < 6000 K) are far too low to produce detectable concentrations of excited halogen atoms. Similarly halogen positive ions are excluded on the basis of their low concentration. Thus, the circumstantial evidence all points toward the assignment of the continua to the halide negative ions.

Next, we can turn to the more positive evidence. There are two strong points and one slightly weaker bit of information which bear directly on the identification. First, we consider the shape of the extinction curves in the region of their thresholds. The outgoing electron in the process (1) makes a transition from a $p$ orbital into either a $d$ wave or an $s$ wave. The $d$-wave process has vanishingly small probability for energies near the threshold energy $E_0$, because the two units of angular momentum in the continuum $d$ state keep its probability maxima relatively far from the atom, and push up the kinetic energy in the region near the atom. Thus, the only “easy” transitions the electron can make into the $d$ states of the continuum are those in which the electron is given some excess kinetic energy by the incident photon. The $s$ states of the continuum, on the other hand, are available even at the threshold since the zero angular momentum imposes no requirement on the kinetic energy. More quantitatively, it has been demonstrated that near the threshold, the cross section for the $s$→$p$ process increases as $(E - E_0)^{1},$
while the $d \rightarrow p$ cross section increases as $(E - E_0)^{3/2}$. Thus, the infinite slope of the extinction curve near the threshold will dominate the appearance of the photo-detachment spectrum of a halide ion. The curves of Figs. 6, 7, and 8 show typical extinction curves in the vicinity of the thresholds. The slopes clearly do not rise with infinite slope, but this is not expected in a system where there is significant broadening of atomic levels from the fluctuating electric fields of ions, for example. The roles of line broadening and ionic fields are discussed below, in connection with the determination of electron affinities and photo-detachment cross sections.

For the moment, it suffices to say that the curvature of the continuous extinction curves in the region of their smooth toes is quite comparable to that of the narrower atomic lines of the alkalis, like the $7p$ and $8p$ lines of Cs and Rb. The absorptions increase extremely rapidly above these toe regions, and have shapes which are entirely consistent with the expected threshold behavior.

![Fig. 5. Microdensitometer tracing showing 10s-6s and 9d-6s absorption lines of Cs, taken from spectrum of CaCl shock. Driver gas, He at 355 psi; driven gas, Ar at 2.15 cm Hg. Tracing is shown uncorrected, but the plate density lies in a region where the correction for nonlinear plate response is negligible.](image)

![Fig. 6. Extinction curve for Cl$^-$ ion taken from typical spectrum, showing the two thresholds. Driver gas, He at 337 psi; driven gas, Ar at 1.7 cm; spectograph, Bausch & Lomb medium quartz; plate, 103-0.](image)

![Fig. 7. Extinction curves taken from three typical shocks, showing the lower-energy threshold of Br$^-$. Conditions, from left to right: CsBr, He at 310 psi, Ar at 1.6 cm Hg; CsBr, H$_2$ at 290 psi; Ar at 2.0 cm Hg; RbBr, H$_2$ at 352 psi; Ar at 2.05 cm Hg (taken from spectrum shown in Fig. 3).](image)

Next, we may examine the separation of the two thresholds associated with a given ion. In the photo-detachment process, the halide ion is in a $^1S_0$ state, so that there is only one initial state possible. If a $p$ electron is removed, the neutral halogen atom may be left in either the $^2P_1$ or $^2P_3$ level. Therefore, there are two final levels for the process, as shown in Fig. 9. The separations of these final states are well known and are included in Table I with the measurements of the threshold separations. In the cases of bromide and chloride, the shapes of the extinction curves are sufficiently similar at their two thresholds, and the background is sufficiently regular, that it was quite easy to measure the threshold separations unambiguously and precisely. Measurements for both these ions were also made with a visual comparator. The upper

![Fig. 8. Extinction curve for I$^-$ in threshold region, taken from spectrum of typical shock of CaI. Driver gas, He at 340 psi; driven gas, Ar at 1.8 cm Hg. Spectrum taken on Hilger medium glass (infrared) spectrograph E414, 103-0 plate. Figure indicates the determination of limits for wavelength of the threshold.](image)
threshold of iodide cannot be located precisely in our present work since it would lie under the region obscured by the 3082, 3092 A doublet of aluminum. Nonetheless, some increase in extinction may occur in that region and is indicated in the table. It is clear that for chlorine and bromine the agreements between the threshold separations and the doublet splittings are reasonably good.

Third, we can look at the relative intensities of the steps in the extinction curves. A simple counting of the allowed transitions shows that exactly one-half of all possible final states can be reached by spin-allowed transitions, and that the two final atomic states will appear in the ratio of their statistical weights, just 2:1, if Russell–Saunders coupling is valid. At present, the measurements of relative intensities do not justify quantitative comparisons, but it is clear that in the spectrum associated with chlorine, the step height ratio is consistent with the value 2:1, and that for bromide their ratio is apparently somewhat higher; no ratio can be quoted with any reliability for iodide. The chlorine and bromide intensities are at least consistent with the interpretation that the final states are the two states of the lowest configuration of neutral halogen atoms.

We are, therefore, led to the conclusion that the two-step continuous absorption spectra are indeed spectra of gaseous negative halide ions and are due to the photodetachment process (1). Confirmation of this assignment has been obtained by comparison with the work of Steiner, Seman, and Branscomb in their independent study of the I⁻ ion.

IV. DISCUSSION

We are prepared now to study the negative halide ions, assuming that the identification of the spectra is established. The immediate problem we investigate, which forms the major topic of the remainder of this paper, is the determination of halogen electron affinities from the absorption spectra. We must answer two questions: (a) How does one determine a threshold from the observed extinction curve; and (b) what corrections must be made for the environmental effects on an ion-absorbing light?

The first of these questions is relatively easy to answer, at least for the degree of precision which we are currently trying to achieve. The second calls for a

| Table I. Threshold separations and fine structure splittings of halogen atoms (eV). |
|---------------------------------|-------|-------|
| Threshold separations          | Fine structure splittings |
| Chloride 0.108±0.007            | 0.1092 |
| Bromide 0.457±0.007             | 0.4568 |
| Iodide (0.950)                  | 0.9424 |

little more discussion. We must investigate the effects of ionic Stark fields, and the measurement of ion densities and temperatures, which in turn raise questions about the establishment of thermal equilibrium and of rates of vaporization, dissociation, and ionization. We can now examine these questions, in order, and then use the information obtained to evaluate electron affinities and cross sections for photodetachment.

A. Threshold Determination

We wish to establish the position of the threshold for photodetachment for a negative ion in its real environment, from the observed extinction curve. We are not yet prepared, nor do we find it necessary for our current purposes to determine theoretical shapes for the bound-free transition cross section near threshold, in the presence of Stark fields. We need only use the knowledge that the cross section is a monotonic increasing function with negative curvature. This is certainly the shape of the curve sufficiently near the threshold. There is further and explicit evidence, from the calculations of Cooper and Martin, that the negative curvature continues for several volts above the threshold. These authors have applied the Klein–Brueckner method to the evaluation of photodetachment cross sections for O⁻, C⁻, Cl⁻, and F⁻. The quantitative agreement between the computed Cl⁻ curve and the observed curve seems to leave something to be desired. Nevertheless, the calculated curves for all four ions do seem to rise monotonically, with negative curvature, for several electron volts above the threshold. The calculations were carried out only for energies above the upper thresholds, so only reflect the sum of the cross sections for the two final states.

The true cross section $\sigma(\nu)$ can presumably be represented as some integral of a spectral density function $g(\xi, \nu)$ taken over a parameter $\xi$ such as the potential near the absorbing ion in an ion atmosphere, the impact parameter in a collision model or a distance in a fixed-atmosphere model. The integrand is just the cross section characteristic of the parameter $\xi$, multiplied by a weight function $\rho(\xi)$. We assume that the shape of $g(\xi, \nu)$ near the threshold is relatively insensitive to $\xi$, and that essentially, a change of $\xi$ just produces a shift of the entire $g(\xi, \nu)$ curve. Next we suppose that the weight function is sufficiently sym-

Fig. 9. Energy levels of halogen atom and halide ion.


metric about a mean value that we may draw this inference: that the point of inflection of the observed curve is an upper limit for the threshold. If \( \rho(\xi) \) were a symmetrical distribution and \( g(\xi, \nu) \) were a square step function, then of course the point of inflection would be the threshold (corresponding to the mean value of \( \xi \)) and at this point the integrated \( \sigma(\nu) \) would be at half-height. If \( g(\xi, \nu) \) is smooth and concave toward the axis, then the point of inflection is above the threshold of mean \( \xi \) and the curve of \( \sigma(\nu) \) is unsymmetrical about the inflection point. The observed inflection points do not occur exactly at the half-height of the thresholds, but at longer wavelengths. Moreover, the curvature of the observed extinction curves is less where it is negative, on the short wavelength side, than on the long wavelength toe where the curvature is positive. The chloride curve shows this asymmetry best, the bromide somewhat less, and the iodide only very slightly. Therefore, the step-function is probably a better good representation of the iodide curve, but is apparently not quite accurate enough to represent the bromide and especially the chloride curves within about 60 Å of their thresholds.

A lower limit of the threshold cannot be selected as unambiguously. If the functions \( g(\xi, \nu) \) rise and flatten quickly as functions of \( \nu \), then the tangent to the \( \sigma(\nu) \) curve at the point of inflection will define a lower limit. If the \((E-E_0)\) behavior is obeyed, or if the \( g(\xi, \nu) \) curves become flat faster than \((E-E_0)\) in the threshold region, then the tangent approximation will be a reasonable one. If the improbable situation were to occur, that the curves had long and gradual slopes over most of the observed range, then some distributions could place the thresholds slightly below the limit set by the tangent. Such behavior seems to be inconsistent with the steeply rising and sharply flattening observed curves.

These two limits define the estimated position of the threshold for a given spectrum within about ±2 Å. If we grant some margin, say another 2 Å, on the low-energy side, the uncertainty in threshold position for a given plate is ±3 Å, and the threshold lies in the region where the optical-density change is about twice the noise level on an average plate.

In addition to the photometric determinations of threshold positions just described, visual measurements of thresholds were made on a comparator. Superposed iron arc spectra provided wavelength comparisons. The agreement between photometric values and visual estimates was good, but their differences exhibited small systematic deviations. The wavelengths selected visually were invariably within an angstrom unit of the point of inflection on the photometric curve, rather than the point we have called the most probable threshold. Figure 8 shows a typical threshold determination.

The variation in threshold wavelengths for a given ion was quite small, consistent with the variation in the environmental corrections. Average threshold wavelengths and corresponding energies for the three ions are:

\[
\begin{align*}
\text{Cl}^-: & \quad 3430 \pm 1 \text{ Å} (3.613 \text{ eV}) ; \\
\text{Br}^-: & \quad 3685.4 \pm 0.6 \text{ Å} (3.563 \text{ eV}) ; \\
\text{I}^-: & \quad 4046.4 \pm 0.6 \text{ Å} (3.063 \text{ eV}) .
\end{align*}
\]

These represent the mean values and deviations of threshold wavelengths as defined by the procedure described above. It is therefore possible that a systematic error could exist due to an incorrect choice of the points which we have called thresholds. Such a systematic error could easily be as large as 1 or 1.5 Å; it seems very unlikely, from the curve shapes, that it could be as large as 3 Å. We have made a corresponding allowance in the uncertainty of the electron affinities quoted in the next section.

B. Environment Correction

The threshold energy for photodetachment of an electron from a negative ion in free space is exactly the electron affinity of the ion. This quantity may be determined directly in crossed-beam experiments, for example, those of Steiner et al.® 24 The experiments described here, however, do not quite achieve such simplicity. In a system composed of dissociated ions and other species, the ions can be described as carrying with them an atmosphere of oppositely charged ions, which gives rise to a potential of mean force, the Debye–Hückel potential, familiar in electrolyte theory. 25 26 The effects of ionic fields on atomic and ionic line spectra have frequently been expressed in terms based directly on the influence of the Debye–Hückel potential. For example, the field distribution function has sometimes been developed from the field of a Debye–Hückel potential. 25 26

In our dissociated salt vapor experiments, an electron is removed from a bound (but slightly broadened) state and left in a positive-energy state, in a region of space where the potential is the sum of the attractive potential of the now neutral atom and the potential due to the surrounding ion atmosphere. We must estimate the effects due to the broadening and to the Debye–Hückel potential, in order to determine electron affinities from observed thresholds.

It seems entirely consistent with the uncertainties in both the threshold measurements and the Debye–Hückel correction that we neglect the effects of ionic fields on the ion ground state. We do this on the

---

24 P. Debye and E. Hückel, Physik. Z. 24, 185 (1923).
following basis. The Stark shift of the ground state of $^1I^-$, for example, would presumably be comparable to or smaller than the shift of a $P$ state of $Cs^0$ having a similar radius, if the $^1I^-$ and $Cs^0$ were placed in identical fields. Then the appropriate states of $Cs^0$ to be used for comparison purposes arise from the $7\rho$ and $8\rho$ orbitals of the valence electron, and correspond to the upper states of some of the transitions we observed. The shifts of the $Cs$ lines arising from these transitions were found to be less than $1 \text{ Å}$ under conditions of these experiments (and may be considerably less); half-widths of these lines are always small compared with the region of uncertainty of the thresholds. It is not possible to give precise half-widths for these intense, low-lying lines because the salt vapor is opaque throughout most of the absorption line; neither the half-height nor the integrated intensity can be determined with any meaningful accuracy. It is possible to say, however, that the ground-state broadening would be small enough to be neglected if the broadening were comparable to the upper limit set by the appropriate cesium lines. In fact, the environment around an ion is expected to show slightly smaller fluctuations than the environment of an atom, just because of the presence of long-range Coulomb forces. Hence the broadening is probably a little less than for comparable atomic levels.

Next, we turn to the determination of the Debye–Hückel potential in which the absorbing ion is immersed. The potential of interest to us is that due to the ion atmosphere at the absorbing ion:

$$x = \frac{-2(\epsilon/D)[\kappa/(1+\kappa a)]}{},$$

where $D$ is the dielectric constant, the inverse Debye length $\kappa = 2\epsilon(\pi\kappa T)^{1/2}$ or $0.144(\pi T)^{1/2}$ cm$^{-1}$, and $a$ is a cutoff length, comparable to an atomic diameter. The dielectric constant of the neutral shocked gas deviates from unity by only about one part per thousand, so we assume $D = 1$. The value of $\kappa$ never exceeded $3 \times 10^5$ in this work, and since $a$ is surely no larger than $10^{-7}$ cm, we drop the product $\kappa a$ from the denominator. The evaluation of $\kappa$ and specifically, of $n$ and $T$, remains to be done.

The ion density has been determined from the widths of the alkali atomic lines. Two related but essentially independent procedures were used. One involved application of the criterion of Inglis and Teller. These authors showed that if first-order Stark broadening could be applied, then the ion density $n$ could be estimated from the "last detectable line" in a series. More specifically, they derived a relation between the total ion density $n$ and the principal quantum number $\mathbf{n}$ of that line for which the line separation becomes equal to the half-width:

$$\log n = 23.26 - 7.5 \log n_{\text{eff}}.$$  

Inglis and Teller also discuss the application to alkaline series. The alkali problem is considered by Mohler, who applies it to cesium. First-order Stark broadening seems to be applicable to the cesium and rubidium series. The hydrogenic principal quantum numbers of the Inglis–Teller formula must, of course, be replaced by the effective quantum numbers of the alkali wave functions. This follows since the size and polarizability of the atomic states of the alkaline, hydrogenic though they are, are still affected by the repulsive cores of inner-shell electrons, which give rise to the quantum defects. The criterion cannot be applied directly to the lines we observed, simply because their intensity was too low to permit us to detect the "last detectable line," the line whose half-width was equal to its separation from the next-higher line. On the other hand, it proved possible to plot linewidth and line separation simultaneously as functions of the effective principal quantum number, and thus to determine, by a short extrapolation, values for $n_{\text{eff}}$ and $n$ appropriate for use in the Inglis–Teller relation. The linewidth curves were plotted as quadratic functions of $n_{\text{eff}}$, since the separation of extreme components of a hydrogenic line in a Stark field varies as $n_{\text{eff}}^2$. In fact,
Table II. Electron affinities of chlorine, bromine, and iodine (eV).

<table>
<thead>
<tr>
<th></th>
<th>Other experimental values</th>
<th>Extrapolated values</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>3.76±0.09(^a)</td>
<td>3.70(^a)</td>
<td>3.628±0.005</td>
</tr>
<tr>
<td></td>
<td>3.70(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.58(^c)</td>
<td>(replaced in later work by assumed value of 3.69)(^b)</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>3.51±0.06(^a)</td>
<td></td>
<td>3.378±0.005</td>
</tr>
<tr>
<td></td>
<td>3.49(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.49±0.02(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.53±0.12(^e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>3.17±0.05(^a)</td>
<td></td>
<td>3.078±0.005</td>
</tr>
<tr>
<td></td>
<td>3.19(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.11(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.13±0.12(^e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.076±0.005(^f)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) See reference 48.  
\(^b\) See reference 51.  
\(^c\) See reference 49; since values for Cl and I were determined relative to Br, we have adjusted our value (column 3) for Br.  
\(^e\) See reference 50.  
\(^f\) See reference 31.  
\(^*\) See reference 52.  
\(^\text{b}\) See reference 53.

The widths of the lines we observed usually increased at a somewhat lower rate. When ion densities were determined from lines as high as 12p, the differences in ion densities from linear and quadratic extrapolations were smaller than the uncertainties associated with line-width measurement, and, when taken together, contributed uncertainties of about 0.1% in the final affinity values. Typical extrapolation curves and the resulting ion densities are shown in Fig. 10.

The second method for determining ion densities is based on the cross section for photodetachment determined by Steiner, Semon, and Branscomb for I\(^-\). At the temperatures and ion concentrations of the systems which were used for affinity determinations, the electron concentrations were negligibly small. Therefore, ion densities could be determined for the iodide spectra just from measurements of the iodide continuous absorption. Moreover, these ion densities, just twice the I\(^-\) concentration, could be used directly to “calibrate" the atomic linewidths. Dimensional considerations alone require that the linewidth \(\delta\) of a line broadened by first-order Stark broadening be related to the ion density \(n\) by the condition\(^{38}\)

\[
\delta = An^4.
\]

It was rarely possible to determine precisely more than two or three half-widths on a single plate. Long-wavelength lines were too intense and shorter-wave-length lines were too weak. As a result, extensive cross-checking could not be achieved. Nevertheless, the agreement of ion density values derived by the two methods gave us some degree of confidence in the densities and also in the extrapolation used in the Inglis–Teller method. In all but a few cases the ion densities derived by the two methods lay within the uncertainties of each. Moreover, other considerations, such as higher temperature and sizeable electron densities invariably accompanied the exceptional cases.

High ion densities approached 5.0±0.5×10\(^{15}\) cm\(^{-3}\), while a spectrum exhibiting low ion density might have a density, typically, of 7±0.6×10\(^{14}\) ions/cm\(^3\).

It was suggested by Ecker and Weizel\(^{38}\) that perhaps a term corresponding to a Madelung ionic crystal potential should be added to the effective potential; it has been argued also by Theimer\(^{37}\) that this term is negligibly small. The controversy has been reviewed recently by Pomerantz.\(^{38}\) We have chosen to neglect the Madelung contribution since \(kT\geq\overline{\varepsilon}\) in all our experiments, and the frequency of the field fluctuations is high compared with atomic linewidths. Therefore, the crystal-like correlation contributions will be thoroughly averaged to zero, and only the solutionlike Debye–Hückel term will remain.

From the ion densities determined from linewidths, and the measured values of \(\log(I_0/I)\), it was possible to get estimates of the cross sections for photodetachment. We obtain

\[
\sigma(\text{Cl}^-) \sim 1.5\times10^{-17} \text{ at } 3360 \text{ Å},
\]

\[
\sigma(\text{Br}^-) \sim 1.2\times10^{-17} \text{ at } 3600 \text{ Å},
\]

and

\[
\sigma(\text{I}^-) \sim 1.5\times10^{-17} \text{ at } 4000 \text{ Å}.
\]

These values must be taken as crude and preliminary. The uncertainties are estimated as about 60%, but the above values are more probably too small than too large. A reasonable uncertainty for Cl\(^-\) might be \(+1.2, -0.5\times10^{17}\) cm\(^2\). Better values can be obtained only after concentration measurements have been made more precise for several species and the question of thermal population distribution has been considered in detail.

Temperature determinations were rather crude by standards applied to much shock-tube work.\(^{22-26}\) Precise knowledge of temperature was not necessary, however, for the determination of the Debye–Hückel correction term. It becomes a sensitive variable in the cross-section determination insofar as it affects ion concentrations. The problems in determining self-consistent temperatures and, thereby, precise concentrations of individual species have led us to postpone any detailed discussion of cross section for future publications.

Temperatures were estimated on the basis of atom concentrations obtained from alkali \(p\)-series line intensities and ion concentrations obtained from alkali line widths. Intensities were measured by plotting
lines from corrected plate density differences and integrating with a planimeter. Oscillator strengths of the atomic lines were then used to determine atom concentrations from the measured areas. Ion concentrations were determined from linewidths as described above. Only high-\(n\) lines were used, e.g., the 11\(p\) of C\(_5\), both because its intensity makes it convenient to measure and because the upper state is sufficiently high in energy that emission from the upper state is negligible. By comparing the observed atom and ion concentrations with concentrations calculated from thermodynamic functions, we were able to make first estimates of temperatures. In most cases, line intensities, linewidths, and negative ion concentrations were consistent with equilibrium conditions at temperatures of 3300\(^\circ\)K \(\pm 600\)\(^\circ\)K. In only a few spectra of very strong shocks were there, simultaneously, markedly decreased negative ion absorption and alkali linewidths still comparable to the widths from weaker shocks. In other words, electron concentrations appeared to be large compared with negative ion concentrations in very strong shocks only. This in itself would place an upper limit on the temperature of about 3600\(^\circ\)K, provided that ionization equilibrium is established. A lower limit on \(T\) can be set if one assumes thermal equilibrium and an upper limit for the photodetachment cross-section. If \(\sigma\) were as high as \(1 \times 10^{-18}\), the computed equilibrium temperature could still be no lower than \(\sim 2400\)\(^\circ\)K.

An attempt was made to estimate temperatures from relative intensities of cesium absorption lines arising from different initial states. Oscillator strengths for many of these lines have been calculated recently. Unfortunately, the uncertainties in the temperatures so determined turned out to be somewhat greater than the uncertainties based on the atom–ion ratios, although the averages of calculated temperatures were comparable.

The Debye–Hückel potentials calculated from the estimated ion densities and temperatures fall between 0.012 and 0.018 V. The uncertainty in any individual potential is about 25%. A typical result, taken from the spectrum of Fig. 2, gives \(n = 1.3 \times 10^{-18}\), \(T = 3300\)\(^\circ\)K and a potential of 0.013 V.

The problem of transients, in both the vaporization and thermal equilibrium processes, will be the subjects of future studies. For the present, we say just a little about the former of these. The vaporization process can be pictured, in a limiting case, as involving instantaneous production of a dust, followed by acceleration and evaporation of the dust particles. In a coordinate system moving with the shocked gas (not with the shock front), the dust particles are decelerated by the viscous medium in which they travel. If there were no vaporization, a cesium iodide particle 2 \(\mu\) in diameter would travel about 15 cm in 400 \(\mu\)sec under conditions of a typical shock. Four-hundred microseconds is a typical interval between the instant the shock front hits the sample and the time the “material front” reaches the observation window; i.e., the time the gas molecules originally in the vicinity of the sample would reach the window. A particle 1 \(\mu\) in diameter can travel about half the 90-cm distance in the same time, and particles smaller than about 0.3 \(\mu\) will travel essentially at the flow velocity, reaching the window with the gas. But, in fact, the particles evaporate as they travel down the shock tube. A lower limit for the vaporization rate can be determined by assuming that it is diffusion controlled. It has been shown by Whitmore and Moser that the simple Langmuir equation is obeyed by small evaporating sodium chloride spheres. From this equation, and typical shock-wave conditions in the gas surrounding the alkali halide dust particles, we estimate that particles 100 \(\mu\) or less in diameter vaporizes in less than 50 \(\mu\)sec, while particles as large as 1 mm in diameter would require perhaps 0.01 sec, which is longer than the entire time of an experiment. Our present picture of the vaporizing salt, therefore, is one in which small particles are vaporized quickly, while large particles, which vaporize slowly, hardly move from their original position, and simply act as sources of salt vapor for the hot argon streaming past.

**B. Conclusions**

The observed spectra and the corresponding Debye–Hückel corrections lead to the electron affinity values shown in the last column of Table II. These may be compared with the values obtained by other investigators; the affinity of iodine determined by photodetachment, values for all three halogens determined by well-known methods of surface ionization, values for bromine and iodine by photoionization, values for thermodynamic cycle calculations, and values from various extrapolation methods. All but the most recent of these have been reviewed by Branscomb. Older values were reviewed by Pritchard.

The affinity values we report are consistently lower than previously reported values, with the exception of the iodine affinity of Steiner, Seman, and Branscomb. The differences are small but significant, according to the uncertainties which previous workers have quoted.

---

The values determined by our direct spectroscopic measurements agree best with the photo-ionization measurements and especially with the photodetachment measurement. As one looks from chlorine to bromine to iodine, one finds a steadily increasing difference between the spectroscopic values and both the Born–Haber cycle values and the values from surface ionization determined by Bakulina and Ionov. (The latter, however, assumed 3.50 eV for the electron affinity of bromine, and determined relative affinities.) Were there a systematic error in the spectroscopic values, from halide–halogen electron exchange for example, we should expect this error to be greatest for iodine. The fact that the iodine value agrees so well with that of Steiner, Seman, and Branscomb appears to be rather strong evidence that our spectroscopic values for Cl and Br are reliable. This is particularly true because of the very dissimilar sources of uncertainty or error in the two kinds of experiments: one, dependent on filter calibrations and an assumed curve shape but carried out with the gaseous ions in an environment very rarefied, and the other, dependent on a rather complex environment correction but based on a sharp spectroscopic threshold. We should point out that the uncertainties in values reported here are due primarily to the uncertainties in temperature and threshold position. The errors which could be associated with ion density determinations would be much more likely to make our estimates of Debye–Hückel potentials too large rather than too small. Therefore, the uncertainties of the electron affinities in column 3 of Table II are not truly symmetrical. The negative signs are definitely more probable than the positive. This is consistent with the direction of the difference in iodide cross-section values found by Steiner, Seman, and Branscomb and ourselves.

In summary, we have determined the electron affinities of chlorine, bromine and iodine from the absorption spectra of the corresponding atomic negative ions. The affinity values are, respectively, 3.628, 3.378, and 3.078 eV, with an uncertainty of 0.005 eV for each.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Lewis Branscomb, Mr. Michael Seman, and Dr. Bruce Steiner for the opportunity to pursue a very stimulating and fruitful cooperation in this work. We would also like to thank Mr. John Cooper and Dr. Philip M. Stone for providing us with their manuscripts prior to publication. We would also like to acknowledge the support of the Directorate of Chemical Sciences, Air Force Office of Scientific Research.