

## V. CONCLUSION

We have seen that  $R_4$  can be applied to first row atoms to give very good approximations to the values of nondynamical correlation energy. In addition the  $Z$  dependence and the role of the exclusion principle are elucidated. The application to the second row shows that it should be possible to obtain estimates of nondynamical correlation in atoms where values for these quanti-

ties are not available.

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## Radiative Capture of Electrons by Chlorine, Bromine, and Iodine Atoms\*

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Absolute intensities were measured in the continuous emission spectrum resulting from electron attachment to the halogen atoms in a shock-heated plasma seeded with sodium halides. The intensity measurements were used to determine new photodetachment cross sections for the negative chlorine, bromine, and iodine ions in the wavelength region between 3000 and 4000 Å. These cross sections are presented here and, where possible, are compared with theoretical and experimental values obtained by other methods. For the case in which the halogen atom is left in the ground state ( $^2P_{3/2}$ ), the present experiments give photodetachment cross sections of  $1.2 \times 10^{-17} \text{ cm}^2$  for  $\text{Cl}^-$ ,  $2.0 \times 10^{-17} \text{ cm}^2$  for  $\text{Br}^-$ , and  $2.2 \times 10^{-17} \text{ cm}^2$  for  $\text{I}^-$  near the detachment thresholds.

## I. INTRODUCTION

When a neutral halogen atom captures a free electron to form a negative ion, the excess energy, consisting of the binding energy and the kinetic energy of the electron, may be transferred to a third body (usually another electron), or it may be converted to radiation. The radiative two-body attachment process is considered herein. Because the free electrons in a plasma have a continuous energy distribution corresponding to

the electron temperature, the spectrum resulting from electron capture is continuous and has a long-wavelength limit specified by the electron affinity of the atoms. The electron-capture continuum is analogous to the positive-ion recombination continuum extending beyond the convergence limit of a particular line series of a neutral atom. The negative halogen ion, however, exhibits no discrete line spectrum, owing to the absence of any energy levels below the detachment energy. For this reason, the electron-cap-

ture continuum shows a sharp long-wavelength cutoff, in contrast with the positive-ion recombination continuum, which merges smoothly into the converging line spectrum at the limit.

The formation of negative ions can occur only if there exists a supply of free electrons. The latter can be created by seeding a plasma with an alkali halide, with the alkali metal supplying the electrons. In the present case, the test gas was seeded with sodium salts and subsequently heated to plasma temperatures by shock compression in a shock tube. Since the halogens have electron affinities between 3.0 and 3.6 eV as compared to the ionization potential of 5.1 eV for sodium, it is evident that at temperatures at which the sodium is moderately ionized the equilibrium value of the negative-ion concentration is quite low. In the temperature range over which the ionization of sodium takes place, the rate of radiative electron capture by the halogen atoms increases with increasing temperature, owing to the increase in the number of free electrons. At the same time the concentration of negative halogen ions decreases owing to the increased collisional detachment rate. It is thus seen that, under the conditions of these experiments, the electron-capture spectra can best be observed in emission at relatively high temperatures, at which the sodium is almost completely ionized and the negative-ion concentration is negligible.

In the past some doubt has been expressed about the possibility of observing the electron-capture continua of the halogens. Early attempts by Franck,<sup>1</sup> Gerlach and Gromann,<sup>2</sup> and Oldenberg<sup>3</sup> to detect these continua in emission were inconclusive, and it was not until this decade that these have been identified experimentally. Much of the earlier work has been summarized by Finkelnburg,<sup>4,5</sup> whereas a more up-to-date review paper on continuous spectra has recently been published by Biberman and Norman.<sup>6</sup>

In absorption, the photodetachment continuum of the  $\text{Cl}^-$  ion has been positively identified in 1961 by Berry, Reimann, and Spokes.<sup>7</sup> Later they also detected the corresponding spectra of the  $\text{Br}^-$  and  $\text{I}^-$  ions<sup>8</sup> and that of the  $\text{F}^-$  ion.<sup>9</sup> A direct study of the photodetachment process for the negative iodine ion was made by Steiner, Seman, and Branscomb,<sup>10,11</sup> who intersected a negative-ion beam with a monochromatic light beam and measured the number of photodetached electrons as a function of light frequency.

In emission, the electron-capture continua were observed by Henning<sup>12</sup> for chlorine and by Berry and David<sup>13</sup> for chlorine, bromine, and iodine; the latter group using the emission from a shock-heated gas seeded with alkali halides, similar to the present experiments. An unusually "clean" emission spectrum, resulting from the radiative electron attachment to fluorine, has been obtained by Popp<sup>14</sup> in an arc discharge.

The experiments described in Refs. 7 to 14 were performed primarily for the purpose of accurately determining the electron affinities of the halogens from the locations of the photodetachment thresholds or the corresponding emission edges. Only a limited effort has been spent to measure the in-

tensity distribution in these continua quantitatively. Consequently the photodetachment cross sections of the negative ions and the corresponding electron-capture cross sections of the neutral atoms are known only approximately. Absolute values of these cross sections have been estimated near the photodetachment threshold for the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions by Berry, Reimann, and Spokes,<sup>8</sup> for the  $\text{F}^-$  ion by Berry and Reimann,<sup>9</sup> and for the  $\text{I}^-$  ion by Steiner, Seman, and Branscomb.<sup>10</sup> Using the crossed-beam technique Steiner *et al.*<sup>11</sup> also made a detailed study of the relative cross sections for  $\text{I}^-$  between 3000 and 4000 Å, and they investigated the threshold shape near 4050 Å with a relatively high spectral resolution. Further work on threshold shapes was performed by Berry, David, and Mackie<sup>15</sup> for the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions, employing shock-tube absorption spectroscopy.

On the theoretical side, photodetachment cross sections near the thresholds have been calculated by Moskvina<sup>16,17</sup> for the  $\text{F}^-$  and  $\text{Cl}^-$  ions. Similar calculations, but for higher electron energies (up to 50 eV) were made by Cooper and Martin.<sup>18</sup> Calculated photodetachment cross sections for the  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions may be found in a recent paper by Robinson and Geltman.<sup>19</sup>

## II. THEORY

At the temperatures considered here the only appreciably populated states of the neutral halogen atom are the ground state ( $^2P_{3/2}$ ) and the first excited state ( $^2P_{1/2}$ ). The energy difference  $\Delta E$  between these states ranges from  $\frac{1}{20}$  eV for fluorine to about 1 eV for iodine. The only known state of the negative halogen ion is its ground state ( $^1S_0$ ). The energy difference  $E_A$  between the ground state of the neutral atom and this negative-ion state is generally referred to as the "electron affinity" of the atom.

Figure 1 shows the possible transitions associated with the radiative capture of an electron of zero energy. The corresponding wavelengths,  $\lambda_1$  and  $\lambda_2$ , represent the long-wavelength limits of the two electron-attachment continua; one due to electron capture by atoms in the  $^2P_{3/2}$  state, the other due to capture by atoms in the  $^2P_{1/2}$  state. For the inverse process of photodetachment the wavelength  $\lambda_1$  corresponds to the lower energy threshold for photons which can photodetach an electron from the negative ion.

These threshold wavelengths, as determined for the halogens by Berry *et al.*<sup>8,9</sup> and Steiner *et al.*,<sup>11</sup> are tabulated in Table I together with the corresponding electron affinities. Since the splitting of the  $^2P$  term is accurately known from the atomic line spectrum, the second threshold  $\lambda_2$  is defined as soon as  $\lambda_1$  is specified.

For wavelengths shorter than  $\lambda_2$  and for an optically thin gas the intensity in the electron-attachment continuum is given by

$$I_c(\lambda) = ABn_e \exp[-hc(\lambda^{-1} - \lambda_1^{-1})/kT], \quad (1)$$

where

$$A = \pi\sqrt{2} h^4 c^2 g_- (\pi m k T)^{-3/2} \lambda^{-5},$$

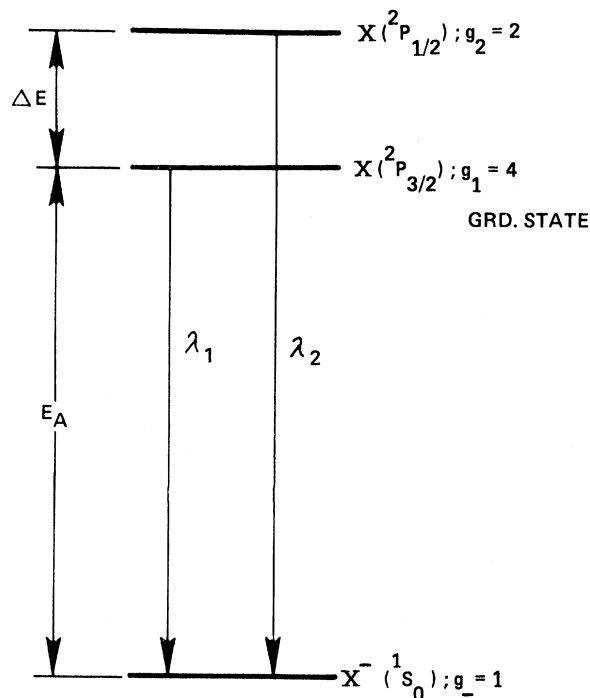


FIG. 1. Energy levels of the halogen atom and the negative halogen ion. (See text.)

and

$$B = \frac{n_1}{g_1} \sigma_{d1}(\lambda) + \frac{n_2}{g_2} \sigma_{d2}(\lambda) e^{\Delta E/kT}.$$

This equation has been derived<sup>20</sup> for the analogous case of the radiative recombination of electrons with positive ions. In this derivation, it has been assumed that the velocity distribution of the free electrons is Maxwellian, and that the thermal velocities of the atoms and ions are negligible compared with those of the electrons. The photoionization cross section has been replaced here by the photodetachment cross sections of the negative halogen ion. In this context,  $\sigma_{d1}$  and  $\sigma_{d2}$  refer to those photodetachment processes which leave the resulting halogen atoms in the  $^2P_{3/2}$  state and the  $^2P_{1/2}$  state, respectively. The sym-

TABLE I. Electron affinities of the halogen atoms and long-wavelength limits of the electron-capture continua.

Atom	Electron affinity $E_A$ (eV)	$\Delta E$ (eV) <sup>a</sup>	$\lambda_1$ (Å)	$\lambda_2$ (Å)
F	$3.448 \pm 0.005^9$	0.0501	$3595 \pm 5^9$	$3544 \pm 7$
Cl	$3.613 \pm 0.003^{8,9}$	0.1092	$3431 \pm 3^{8,9}$	$3330 \pm 4$
Br	$3.363 \pm 0.003^{8,9}$	0.4568	$3686 \pm 3^{8,9}$	$3245 \pm 4$
I	$3.059 \pm 0.002^{11}$	0.9424	$4052 \pm 3^{11}$	$3098 \pm 4$

<sup>a</sup>C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949, 1952, and 1958), Vols. I, II, and III, respectively.

bol  $I_c(\lambda)$  represents the energy radiated in unit time by a unit volume of gas in unit wavelength interval at the wavelength  $\lambda$ . The number density of electrons is expressed by  $n_e$ , the number density of halogen atoms in the  $^2P_{3/2}$  and  $^2P_{1/2}$  states by  $n_1$  and  $n_2$ , respectively. The  $g$ 's are the statistical weights of the energy levels involved (see Fig. 1). The symbols  $m$ ,  $k$ ,  $h$ , and  $c$  have their usual meaning;  $T$  is the electron temperature. For wavelengths between  $\lambda_1$  and  $\lambda_2$  Eq. (1) is valid if  $\sigma_{d2}$  is taken to be zero there.

Under conditions of thermodynamic equilibrium,  $T$  is the equilibrium temperature, and the distribution of halogen atoms among the energy states is Boltzmannian, i. e.,

$$n_1/g_1 = (n_2/g_2) \exp(\Delta E/kT). \quad (2)$$

In this case Eq. (1) can be inverted, so that the sum of the photodetachment cross sections can be given explicitly in terms of  $I_c$ ,  $T$ ,  $n_e$ , and  $n_1+n_2$

$$\sigma_{d1}(\lambda) + \sigma_{d2}(\lambda) = C(\lambda, T) I_c(\lambda) / n_e (n_1 + n_2), \quad (3)$$

where

$$C = A^{-1} (g_1 + g_2) e^{-\Delta E/kT} e^{hc(\lambda^{-1} - \lambda_1^{-1})/kT}.$$

Hence, by measuring the intensity at a specific wavelength in the electron-capture continuum, the corresponding photodetachment cross section ( $\sigma_{d1} + \sigma_{d2}$ ) can be found if  $T$ ,  $n_e$ , and  $n_1+n_2$  are known. The photodetachment cross sections of the negative ion are related to the electron-capture cross sections of the neutral atom by Milne's<sup>21</sup> relation. According to this relationship the electron-capture cross section  $\sigma_{c1}$  of the ground-state atom is given by

$$g_1(mv)^2 \sigma_{c1} = g_-(h/\lambda)^2 \sigma_{d1}. \quad (4)$$

Similarly, that of the neutral atom in the first excited state is given by

$$g_2(mv)^2 \sigma_{c2} = g_-(h/\lambda)^2 \sigma_{d2}. \quad (5)$$

### III. EXPERIMENTAL

The work presented here was made possible only after a previous set of experiments was completed using the same shock tube and instrumentation. These previous experiments, reported elsewhere,<sup>20</sup> dealt with the continuum radiation resulting from the recombination of free electrons with positive sodium ions. In the present experiments this sodium radiation partially overlapped the electron-capture continua of the halogens and had to be subtracted from the observed emission. Although the apparatus has been described in detail before,<sup>20</sup> a short description of the experimental arrangement is repeated here.

The test gas, which was argon seeded with NaCl, NaBr, or NaI, was heated to approximately 6000°K by shock compression in a stainless-steel shock tube, having a 4.5-m-long section and an

internal diameter of 7.6 cm. The test conditions were achieved behind the reflected shock near the end of the driven section. The equilibrium temperature for these conditions was calculated from the incident shock velocity, which was determined by timing the arrival of the shock at a series of heat-transfer gauges mounted in the shock-tube wall. The seed material was introduced by boiling it off an electrically heated tantalum boat, while passing the argon over it in the process of loading the driven section. The mole fraction of seed material added in this way could be calculated from the observed sodium line intensities and was found to be approximately  $10^{-3}$ .

The radiation emitted by the shock-heated gas could be observed through 6-mm-thick sapphire windows, which were mounted in the wall of the shock tube 2.5 cm from the end of the driven section. Two spectrometers, receiving light from the same volume of gas, were used to analyze the emitted radiation. Both instruments were calibrated *in situ* against the known energy emission from a standard tungsten-filament lamp. One of the spectrometers was a  $\frac{1}{3}$ -m  $f/4$  Ebert-type grating instrument with a seven-channel output, which was used to measure simultaneously seven intensities in the electron-capture continuum. The wavelength channels were 15 Å wide and spaced 90 Å center to center. They were formed by seven  $0.5 \times 5$ -mm<sup>2</sup> slits in a mask at the image plane of the instrument. The light was conducted from these slits to quartz-window photomultipliers (EMI 9526B-S13 Response) by means of specially designed light guides, the walls of which were made from aluminized plastic strips.

The second instrument was a Hilger-Watts constant-deviation prism monochromator and was employed to measure the intensity of the sodium doublet at 5150 Å ( $6s^2S_{1/2}$  to  $3p^2P_{1/2, 3/2}$ ). The measured intensity of this doublet was used to determine the number density of neutral sodium atoms. In this determination absorption was neglected, and the doublet oscillator strength,  $g_l f$ , was taken to be 0.024 (Allen<sup>22</sup>).

Optical filters were used to screen out the intense yellow resonance radiation of sodium. This afforded a significant reduction in the stray-light background. A Corning 7-59 blue filter was used in series with the seven-channel grating instrument, and an interference filter with a 170 Å wide transmission band at 5200 Å was used in conjunction with the prism monochromator.

For all tests, the temperature behind the reflected shock fell between 6000 and 6500°K. In this temperature range the following assumptions were considered to be valid.

(1) All sodium halide molecules were dissociated, and the equilibrium concentration of molecular species of any kind was negligible. This was taken to apply specifically to such diatomic species as Na<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> and to impurity molecules.

(2) The number of negative and positive halogen ions was negligible compared with the number of neutral halogen atoms. (For example, at 6250°K and for  $n_e = 10^{16}$  cm<sup>-3</sup>, the Saha equation indicates

that the ratio of negative chlorine ions to neutral chlorine atoms is  $10^{-3}$ , whereas the ratio of positive chlorine ions to neutral chlorine atoms is  $10^{-5}$ . The corresponding numbers for iodine are  $3 \times 10^{-4}$  and  $10^{-3}$ .)

(3) Practically all halogen atoms were in either the ground state or the first excited state. (This condition is fulfilled because the next-higher excited states for Cl, Br, and I lie 8.9, 7.9, and 6.8 eV above the respective ground states.)

(4) All the sodium existed in the form of neutral atoms and singly ionized ions.

(5) The number of argon ions was small compared with the number of positive sodium ions.

(6) Any atomic impurities in the test gas were present in negligible amounts, or had ionization potentials considerably above that of sodium.

If assumptions (1) to (4) are accepted, then it follows that

$$n_1 + n_2 = n_{\text{Na}} + n_{\text{Na}^+} \quad (6)$$

Assumptions (2), (4), (5), and (6) are necessary for making the statement that all free electrons resulted from the ionization of sodium, and that no electrons were lost owing to the formation of negative ions. In this case

$$n_e = n_{\text{Na}^+} \quad (7)$$

Before each test the shock tube was evacuated to a pressure of less than  $10^{-4}$  Torr. After purging the tube twice with pure argon, the driven section of the shock tube was filled with argon seeded with sodium halide smoke, until the pressure was 12 Torr. The shock-tube driver was then loaded with 10 atm of helium, which was sufficient to rupture the aluminum diaphragm. Under these conditions the reflected shock temperature was typically around 6250°K, and the number densities of particles behind the reflected shock were as follows:

Number of positive sodium ions and electrons,

$$n_{\text{Na}^+} = n_e = 4 \times 10^{15} \text{ cm}^{-3};$$

Number of neutral sodium atoms,

$$n_{\text{Na}} = 2 \times 10^{14} \text{ cm}^{-3};$$

Number of halogen atoms,

$$n_1 + n_2 = 4.2 \times 10^{15} \text{ cm}^{-3};$$

Number of argon atoms,

$$n_{\text{Ar}} = 4 \times 10^{18} \text{ cm}^{-3}.$$

A typical oscilloscope recording of the observed continuum radiation from the shock-heated gas is shown in Fig. 2 for two particular wavelength channels. The oscilloscope traces represent intensity as a function of time. Time *A* marks the arrival of the reflected shock at the test-section window. The test period is terminated at *B* by the arrival of a wave, which resulted from the interaction of the reflected shock with the helium-argon contact surface. When reducing the data it was assumed that 250 μsec after the arrival of the reflected shock the plasma was in thermo-

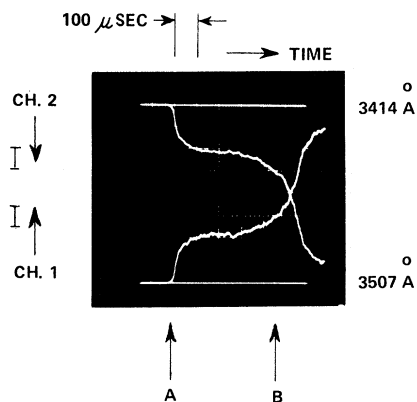


FIG. 2. Time history of the continuum radiation from NaBr at two wavelengths.

dynamic equilibrium. The intensities observed at this instant were used for deriving the cross sections reported in Sec. IV.

The normal-shock relations were used to calculate the equilibrium temperature behind the reflected shock from the measured shock speed. The effects of the sublimation of the sodium halide smoke particles, of the dissociation of the sodium halide molecules, and of the ionization of the sodium atoms on the equilibrium temperature were calculated to be approximately 2%. Suitable corrections were applied.

On the basis of this equilibrium temperature, the number of sodium atoms in the  $6S$  state was then determined from the measured intensity of the sodium doublet at  $5150 \text{ \AA}$ . A Boltzmann distribution of sodium atoms among the available energy states was assumed in order to calculate  $n_{\text{Na}}$ . Application of the Saha equation then gave  $n_e n_{\text{Na}^+}$ , which according to Eq. (7) is equal to  $n_{\text{Na}^+}^2$  or  $n_e^2$ . The number density of halogen atoms was then obtained from Eq. (6). These number densities, together with the intensities measured in the electron-capture continuum, were then used to calculate the photodetachment cross sections. The values of  $I_C(\lambda)$  were found by subtracting from the measured intensities the known contributions<sup>20</sup> resulting from radiative recombinations of electrons and positive sodium ions into the  $3^2P_{1/2,3/2}$  state of sodium.

#### IV. RESULTS

The experimentally determined photodetachment cross sections for the negative ions of chlorine, bromine, and iodine are presented in Figs. 3 to 5 for the wavelength range between 3000 and 4000  $\text{\AA}$ . The wavelengths of the photodetachment thresholds are marked by arrows and the spectroscopic terms of the corresponding neutral states. For wavelengths between the two thresholds ( $\lambda_1 > \lambda > \lambda_2$ ), the measured cross section  $\sigma_d$  refers to  $\sigma_{d1}$  only. For wavelengths shorter than  $\lambda_2$  the cross section  $\sigma_d$  represents the sum of  $\sigma_{d1}$  and  $\sigma_{d2}$ . (The units are mega-

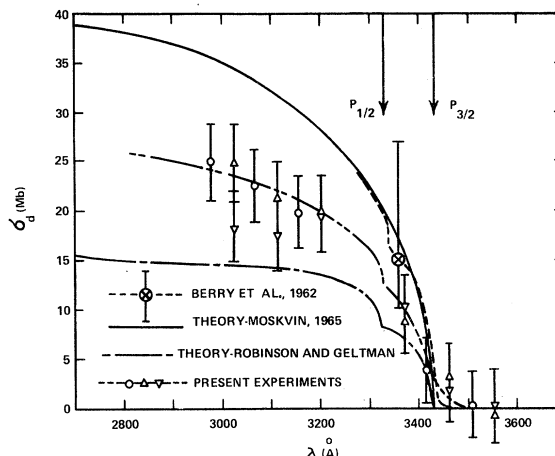


FIG. 3. Photodetachment cross sections for the negative chlorine ion.

barns;  $1 \text{ Mb} = 10^{-18} \text{ cm}^2$ .) Different symbols refer to different shock-tube runs. No meaningful measurements could be made around 3300  $\text{\AA}$ , because of the presence at 3302  $\text{\AA}$  of the second member of the principal series of the sodium line spectrum. The error bars represent the estimated magnitudes of the random errors introduced by the uncertainties in the shock-speed measurements and in the calibration of the spectrometers.

In Fig. 3 the results for  $\text{Cl}^-$  are compared with those obtained by Berry, Reimann, and Spokes<sup>8</sup> (dashed curve) from the absorption spectrum of a shock-heated argon plasma seeded with  $\text{CsCl}$ . Berry *et al.* quote an absolute value of 15 Mb, with an uncertainty of +12 and -5 Mb, for the photodetachment cross section at 3360  $\text{\AA}$ . They obtained this value by estimating the negative-ion concentration from the widths of the Stark-broadened absorption lines of cesium. The relatively large uncertainty quoted is a direct consequence of the difficulty with which these linewidths can be interpreted quantitatively.

The solid curve in Fig. 3 is based on calculations

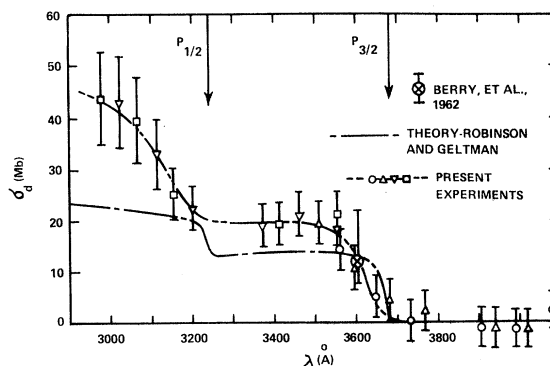


FIG. 4. Photodetachment cross sections for the negative bromine ion.

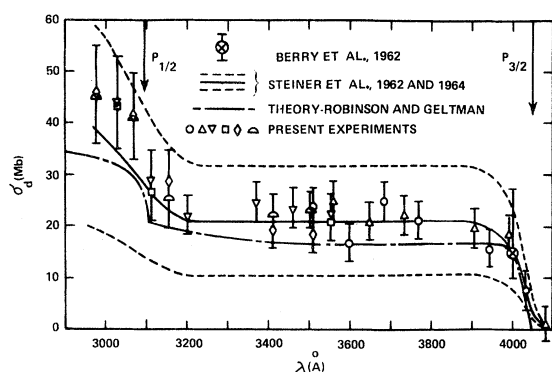


FIG. 5. Photodetachment cross sections for the negative iodine ion.

by Moskvin,<sup>17</sup> who used the self-consistent field approximation for the wave functions of the bound states. These calculations agree rather well with the measurements of Berry, Reimann, and Spokes. The present results, on the other hand, indicate that Moskvin's cross sections may be somewhat large.

There exists no inconsistency between the present measurements and the results of Berry *et al.*, if due allowance is made for the possible experimental errors. The curve fitted through the present data points has been drawn in such a way as to simulate the shape of the threshold region observed by Berry. The fact that the threshold is not sharply defined for the present conditions may be attributed to Stark broadening of the energy states involved in the electron-capture process.

The results for the negative bromine ion are shown in Fig. 4. The continuous curve drawn through the experimental points indicates two distinct thresholds, which coincide with the values of  $\lambda_1$  and  $\lambda_2$  quoted in Table I. The cross sections for  $\text{Br}^-$  are in excellent agreement with a value found by Berry *et al.*<sup>8</sup> at 3600 Å. The experimental curve appears to be relatively flat between 3500 and 3200 Å and seems to increase monotonically with decreasing wavelength below  $\lambda_2$ .

The photodetachment cross sections obtained for the negative iodine ion (Fig. 5) agree well with those found by Berry *et al.*<sup>8</sup> and by Steiner *et al.*<sup>10,11</sup> The detailed measurements of Steiner, Seman, and Branscomb,<sup>11</sup> who employed a crossed-beam technique, are represented here by the solid curve.<sup>23</sup> The dashed curves denote the upper and lower bounds for these cross sections based on an uncertainty of  $\pm 50\%$  for the absolute magnitudes as quoted by Steiner *et al.*<sup>10</sup> Again the cross-section curve is relatively flat between the thresholds, which for iodine are separated by almost 1000 Å. Apart from the different threshold separation, the cross-section curves for  $\text{Br}^-$  and  $\text{I}^-$  are very similar in shape and magnitude.

Theoretical curves calculated by Robinson and Geltman<sup>19</sup> are also shown in Figs. 3 to 5. For all three halogens these calculated cross sections are consistently smaller than the observed ones.

For bromine and iodine  $\sigma_{d1}$  reaches a plateau

within approximately 150 Å of  $\lambda_1$ . On account of this behavior one expects  $\sigma_{d2}$  to change similarly near  $\lambda_2$ . Furthermore, one would expect the step heights of the cross-section curve at the two thresholds to be related to each other in terms of the energies and the statistical weights of the energy states involved in the transitions. If it is assumed that, for a given electron energy, the capture cross section of a halogen atom in the  $^2P_{1/2}$  state is identical with that of a halogen atom in the  $^2P_{3/2}$  state, then Eqs. (4) and (5) yield the following prediction for the cross-sections ratio:

$$\frac{\sigma_{d1}(\lambda_a)}{\sigma_{d2}(\lambda_b)} = \frac{g_1}{g_2} \left( \frac{E_A + \Delta E + \frac{1}{2}mv^2}{E_A + \frac{1}{2}mv^2} \right)^2, \quad (8)$$

where the cross sections are those at the wavelengths  $\lambda_a$  and  $\lambda_b$ , which in turn are related by

$$1/\lambda_a - 1/\lambda_1 = 1/\lambda_b - 1/\lambda_2. \quad (9)$$

Close to the thresholds  $\lambda_1$  and  $\lambda_2$  the electron energy is small compared with  $E_A$ , and the ratio of cross sections, as given by Eq. (8), can be calculated from the data in Table I. For  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  this ratio becomes 2.13, 2.57, and 3.42, respectively. Berry *et al.*<sup>8</sup> found that the step heights of  $\sigma_{d1}$  and  $\sigma_{d2}$  near their respective thresholds are approximately in the ratio of 2 to 1 for chlorine. For bromine they report observing a cross-section ratio greater than 2, which would be consistent with Eq. (8). No ratio was quoted for iodine.

The present results for bromine and iodine indicate that  $\sigma_{d1}$  and  $\sigma_{d2}$  are of similar magnitudes. This aspect of this work is at variance with Berry's observations and with the assumption of equal capture cross sections for the  $^2P_{3/2}$  and  $^2P_{1/2}$  states. However, because it was not possible to determine  $\sigma_{d1}$  and  $\sigma_{d2}$  separately, and because of the lack of cross-section data for wavelengths shorter than 3000 Å (the present experiments were limited to wavelengths longer than 3000 Å because of the calibration problem), no definite statement can be made at this time about the specific behavior of  $\sigma_{d2}$ .

A remark should be made at this point about the applicability of the thin-gas assumption with respect to the radiation measured herein. In the wavelength region between 3000 and 4000 Å the continuous absorption due to photodetachment of electrons from negative halogen ions is negligible because of the small number density,  $n_-$ , of negative halogen ions. Over an optical path length of 1 cm, the probability of absorption due to this cause is given by  $\sigma_d n_-$ , which is of the order of  $10^{-4}$  for the conditions encountered in the tests. The continuous absorption due to photo-ionization of neutral sodium atoms in the  $3P$  state is similarly negligible. A small error of a few percent may have been introduced, however, by the possible lack of complete transparency for the sodium doublet at 5150 Å. This error, which would make the determined cross sections too large, has been discussed in Ref. 20, where it is shown that the resulting error in the cross sections is smaller

than 12% and possibly negligible for the present conditions.

### V. CONCLUSIONS

The electron-capture continua of the halogens have been studied, and absolute photodetachment cross sections have been derived for the negative ions of chlorine, bromine, and iodine. The magnitudes and shapes of the cross-section curves are in general agreement with those obtained by absorption studies and by crossed-beam experiments. There exists no doubt about the identity of the observed continua because of the appearance at the predicted wavelengths of the two distinct thresholds, characteristic for the electron-capture continua of the halogens. The known continuum due to the recombination of electrons with positive sodium ions has been subtracted from the measured intensities. No other continuous radiation was observed, as can be noted from the fact

that the photodetachment cross sections go to zero for wavelengths greater than  $\lambda_1$ .

The absolute magnitudes of the measured cross sections are based on a multiplet oscillator strength  $g_{if}$  of 0.024 for the sodium doublet at 5150 Å. The cross sections are directly proportional to this number. Consequently, the uncertainty in this number is reflected in the present data and should be added to the experimental error indicated in Figs. 3 to 5. If future work should disclose a different value for the oscillator strength of this sodium doublet, the present cross sections should be adjusted accordingly.

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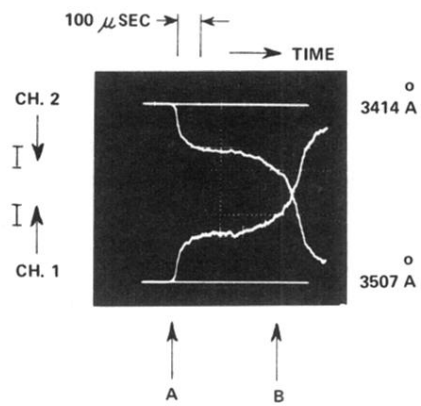


FIG. 2. Time history of the continuum radiation from NaBr at two wavelengths.