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RADIATIVE CAPTURE OF ELECTRONS BY HALOGEN ATOMS

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RADIATIVE CAPTURE OF ELECTRONS BY HALOGEN ATOMS

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We wish to report the direct spectroscopic observation of radiative capture of electrons by the free gaseous halogen atoms Cl, Br and I. The spectra were obtained from emission produced by alkali halides vaporized and dissociated by shock-heating. The sharp onsets of radiation due to capture of electrons of zero energy are clearly visible. The radiation intensity dependence near onset is, within experimental uncertainty, consistent with the photodetachment spectra, the Wigner Threshold law and microscopic reversibility; that is, the capture cross section becomes very steep at threshold and the light intensity appears to rise as $(\nu - \nu_0)^{\frac{3}{2}}$ as a function of ν . The continua are identified by shape and threshold wavelength, and in the case of Cl and Br, by the presence and wavelength of continua due to capture of electrons by atoms in their excited $^2P_{\frac{3}{2}}$ states. Threshold wavelengths are: 3427 ± 4 and 3327 ± 4 Å for Cl; 3688 ± 4 and 3249 ± 3 Å for Br, and 4046 ± 4 Å for I. These are in good agreement with the photodetachment thresholds. Capture cross sections for electrons with energy of 0.025–0.035 eV are approximately 10^{-21} cm².

We wish to report the observation of emission spectra due to the radiative capture of low-energy electrons by the gaseous halogen atoms Cl, Br and I. The spectra are continua with sharp onsets, as expected from the photodetachment spectra of these same species¹⁻³. We have assigned the spectra from their qualitative shapes, from the values of their wavelengths at onset, and in the case of Cl and Br, from the position and relative intensity of the second step arising from radiative capture by excited ($^2P_{\frac{3}{2}}$) atoms.

Laboratory observations of radiative capture continua in emission spectra of arcs⁴⁻⁷ and of shocked gases^{8,9} have been reported. However, to our knowledge, no thresholds due to s-wave capture have been observed heretofore. Direct observation of the capture of electrons of zero kinetic energy into the lowest available p-level of groundstate atoms has now proved possible in our work.

The sources of our emission spectra are the vaporized, dissociated alkali halides present in the hot gases behind shock waves. In its simplest form, the apparatus is essentially the same as that used for photodetachment studies^{1,2},

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except that no spectral flash is necessary and the mirrors of the multiple pass cell are arranged to trap light and send it to the spectrograph slit. Typical conditions for the production of the emission continua are 320–400 psi driving pressure of H_2 , 2.1 cm Hg of Ar as the driven gas, a shock velocity (after the shock has struck the sample) of 1.6 mm/microsecond and a salt sample of 1.4 millimoles supported on aluminum foil.

Two types of emission spectra have been taken. In the earliest observations, a Bausch and Lomb medium quartz spectrograph collected light emitted during the entire duration of the shock. A time-integrated spectrum exhibits the thresholds, but as the following discussion shows, it is difficult to determine a meaningful attachment coefficient from such a spectrum. We have therefore taken subsequent spectra using a high-speed spectrograph having a rotating drum camera body. The highest time resolution obtained in the capture spectra has been about 20 microseconds. Time resolved spectra

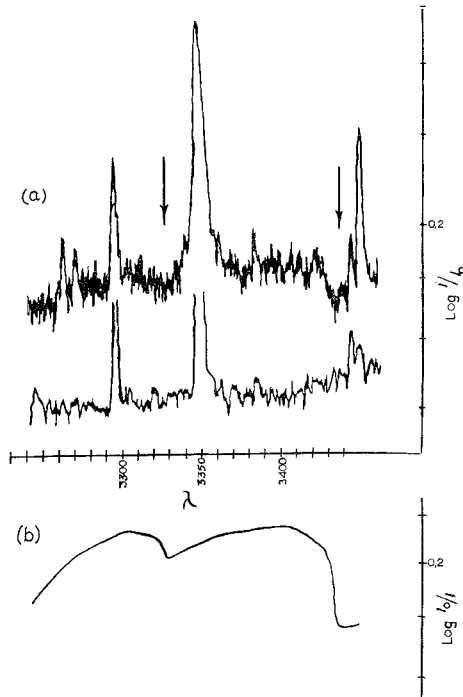


Fig. 1. a) Microdensitometer tracings of emission spectra showing two continuum onsets due to electron capture by Cl atoms (upper), and a comparison (lower). The upper tracing is taken from a shock in RbCl; the lower, in RbI. Conditions for both as given in the text. b) Relative intensity curve based on the tracings of a); and a plate calibration curve.

The wavelength scale is the same for a) and b).

were taken on Eastman Kodak 1-0 35 mm film; time-integrated spectra were taken on 103-0 and 1-0 plates. Both were developed five minutes in D-19 developer. Slit widths for both sorts of spectra corresponded to about 1 \AA , narrow enough that Stark broadening of the alkali lines was easily noted. Microdensitometer tracings were made on a Leeds and Northrop Knorr-Albers microdensitometer.

Figure 1a is a tracing of the microdensitometer record of a typical spectrum, from RbCl in this case, together with a comparison spectrum (actually taken from a shock through RbI). Figure 1b is the curve of the logarithm of the

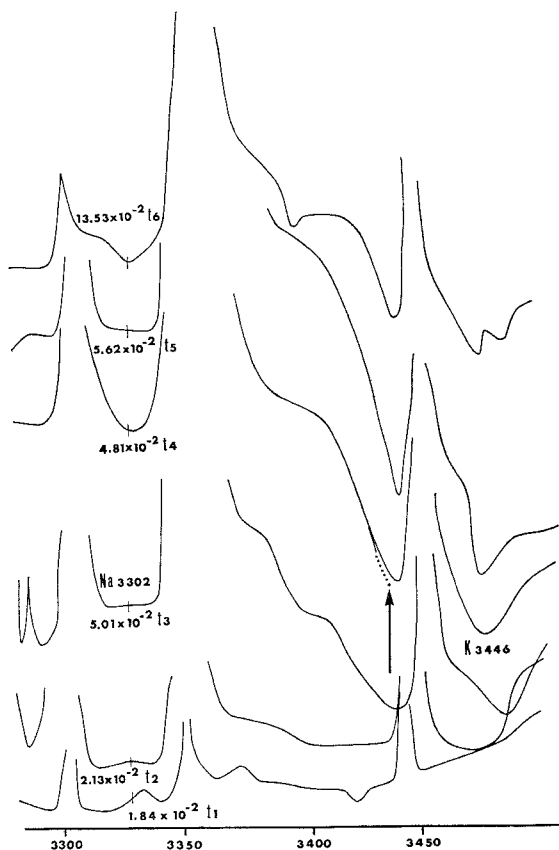


Fig. 2. Relative intensity curves showing onset of continuous emission due to radiative capture of electrons by chloride atoms. These curves were made from corrected microdensitometer tracings of a film from the rotating drum spectrograph, and correspond to successive times (reading upward) approximately $20 \mu\text{sec}$ apart in the laboratory frame. Shocked salt: RbCl; driving (H_2) pressure, 400 psi; initial argon pressure, 2.0 cm Hg. The indicated threshold position is determined as discussed in refs.^{1, 2}.

relative intensity, taken from the measurements of figure 1a. Figure 2 shows the curves of the relative intensity itself, taken from measurements of a time-resolved spectrum of RbCl vapor*. The relative intensities of figures 1 and 2 were derived with the aid of plate calibrations made with a seven-step neutral density filter. The two steps in the emission spectrum, corresponding to capture of zero-energy electrons by ${}^2P_{\frac{3}{2}}$ and ${}^2P_{\frac{1}{2}}$ chlorine atoms, are clearly visible. The onsets for Br and I have the same appearance in their corresponding wavelength regions.

The intensity of emitted light in radiative capture can be expressed conveniently in terms of the electron wave number k as

$$I(k) dk = \alpha(k) n_x n_e(k) dk \sim \alpha(k) n_x n_e k^2 \exp(\beta h^2 k^2 / 2m) dk \quad (1)$$

or in terms of the frequency ν of emitted light as

$$I(\nu) d\nu \sim \alpha(\nu) (\nu - \nu_0)^{\frac{1}{2}} n_x n_e \exp[\beta h(\nu - \nu_0)] d\nu. \quad (2)$$

We let $\alpha(= \sigma_{\text{att}} v_e)$ be the attachment coefficient, n_x and n_e be the concentrations of atoms and electrons, m be the electron mass and β be $1/kT$.

The dependence of I on T , through the Boltzmann factor for electron energies, is the source of difficulty in the interpretation of time-integrated spectra. The time-integrated spectra superpose emission from a variety of conditions, so that no well-defined ion densities or attachment coefficients can be derived from them. On the other hand, the time-resolved spectra presumably show the system in local thermal equilibrium and therefore do permit derivation of meaningful attachment coefficients. The question of thermal equilibrium is now under investigation.

For the attachment transition of an electron from an s-wave into a p-level, α has a finite value at $k = 0$ ¹⁰. Because the interaction between the electron and the atom varies as $-\gamma^2/r^4$ at long distances, the phase shift expression $k \cot \delta$ contains a term linear in k , as well as constant and quadratic terms¹¹. From this we conclude that the leading terms in the attachment coefficient give it a form near $k = 0$ of

$$\alpha(k) = \frac{C}{\lambda^3} [A_0 + A_1 k + \dots]. \quad (2)$$

The constant C depends on the ratio of the degeneracy of the negative ion and to that of the neutral atom. In the effective range formalism, A_0 can be

* All the curves in figs. 1 and 2 have the same vertical dimension but scales are shifted for clarity; fiduciary mark for each curve indicates the position it would have if all the curves were on the same scale.

written as $(aI_0 - I_1)^2$, where a is the scattering length and I_0 and I_1 are each combinations of two atomic radical integrals. Similarly, A_1 is given by $\frac{2}{3}\pi\gamma^2 I_0(aI_0 - I_1)$. In principle one can use these relationships to derive scattering lengths and atomic polarizabilities, γ^2/e^2 . The data we have obtained so far, while entirely consistent with (2), do not yet allow evaluation of a limiting slope and intercept from plots of the intensity I , in the form I/k^2 vs. k . From photodetachment cross sections^{2,3}, the attachment cross sections, are found to be about 10^{-21} cm² for all three substances, about 200–300 cm⁻¹ above the onsets of the continua.

The continua appear to have small toe regions, due probably to Stark broadening. If we estimate the position of the onsets in the same manner used for the photodetachment thresholds¹, the wavelengths for emission and absorption are in excellent agreement, ± 3 Å. The presence of many weak emission lines in the spectra has made it hard to study with precision the region ± 4 Å around the thresholds. Further investigations with time-resolved spectra will hopefully reduce this difficulty. We report our observed wavelengths for the onsets of the radiative attachment continua as

$$\text{Cl: } 3427 \pm 4\text{Å and } 3327 \pm 4\text{Å};$$

$$\text{Br: } 3688 \pm 4\text{Å and } 3249 \pm 3\text{Å};$$

$$\text{I : } 4046 \pm 4\text{Å}$$

The onset of the second transition of iodine, $\text{I}(^2\text{P}_{3/2}) + e \rightarrow \text{I}^-$, has not been identified unambiguously in the emission spectra, although it is definitely seen in photodetachment². The splittings we observe for Cl and Br are 877 ± 40 cm⁻¹ and 3660 ± 40 . The actual fine structure separations of these atoms are 881 and 3685 cm⁻¹ (ref. ¹²).

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