Electron photodetachment cross sections of Cl⁻ and Br⁻ †

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The absorption spectra of the negative ions of chlorine and bromine have been observed in shock-heated vapors of CsCl and CsBr, respectively. The photodetachment cross sections of Cl⁻ and Br⁻ have been measured from their threshold values down to 2000 Å. The results are found to be in good agreement with the calculated values of Robinson and Geltman.

I. INTRODUCTION

The photodetachment of negative ions is important in many areas of physics, e.g., astrophysics, atmospheric, plasma, and laser physics. Halogen atoms and their ions play an important role in the physics of current laser systems, e.g., HF, DF, and KrF.

There have been several theoretical calculations[1-3] and measurements[4-9] of photodetachment from halogen negative ions. The disagreement between what seems to be the best calculation to date (Ref. 1) and the measurements has been as much as a factor of 2. Since the theory is claimed[10] to be more accurate than this (i.e., ±20%) we have undertaken a systematic experimental study of the halogen negative ions. The measurements reported here for Br⁻ and Cl⁻ show good agreement with the theoretical calculations, as did our previous measurements on F⁻ (Ref. 8) and I⁻ (Ref. 9).

II. APPROACH

The work of Berry *et al.*[5] has shown that all of the cesium halides will thermally dissociate almost exclusively into the ionic rather than the neutral branch. This is because the potential energy curves for the neutral atoms and the ions cross at large internuclear separation (CsF: 61.8 a.u.; CsCl: 97.1 a.u.; CsBr: 51.3 a.u.; CsI: 32.8 a.u.).[5] Since the electron spends most of its time on the halogen it cannot make the jump to the cesium ion as the molecule dissociates, even though this would be the lower energy state. This allows one to produce very high (~10^{16} cm⁻³) densities of negative halogen ions.
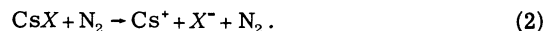
The cesium halides are introduced into the shock tube as 0.05-μm particles mixed with nitrogen. This mixture is formed by passing nitrogen over molten cesium halide and allowing the vapor of the salt to self-nucleate. A system similar to the one used in this experiment for condensing CsBr and CsCl was described earlier.[11] It was used for introducing CsF into the shock tube. The previous-

ly described system can be used for these experiments, since all the cesium halides have similar physical properties (e.g., melting points are all within 63 °K of each other and boiling points are within 50 °K of each other). They are all white powders at room temperature, and, except for the fact that they are hygroscopic, they present little problem in handling.

The gas-particle mixture is subjected to incident followed by reflected shock heating, causing the CsX (X = Br, Cl) to ablate and then dissociate. The final gas temperature is ~5000 °K. Thus in the incident shock

$$\text{Cs}X_{\text{(particles)}} + \text{N}_2 \rightarrow \text{Cs}X_{\text{(gaseous)}} + \text{N}_2 , \qquad (1)$$
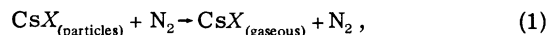
and in the reflected shock

$$\text{Cs}X + \text{N}_2 \rightarrow \text{Cs}^+ + X^- + \text{N}_2 . \qquad (2)$$

This method allows the production of ion densities [X^-] on the order of 10^{15}–10^{16} cm⁻³.

The amount of absorption due to X^- is obtained by monitoring its absorption continuum. Ultraviolet light from a xenon flash lamp is analyzed with a double $\frac{1}{4}$-m Jarrell-Ash monochromator together with a photomultiplier (S13 surface). The absorption is due to the photodetachment of X^-,

$$X^- + h\nu \rightarrow X + e . \qquad (3)$$

The photodetachment cross-section measurements are made just behind the reflected shock front. This is because the [X^-] produced after the reflected shock front does not remain constant, since at the high temperature of our experiments equilibrium calculations predicts very little X^-. Thus the nonequilibrium dissociation [reaction (2)] is followed by a decay of the X^- via collisional detachment[12] and some recombination with the Cs⁺. Just behind the reflected shock front the [X^-] and [Cs⁺] are equal (later, at equilibrium, they are not equal).

The [Cs⁺] is obtained by observing Cs⁺ + e free-bound recombination radiation at 4215 Å at equilibrium. Since the cross section for this process has been measured,[13,14] and since we have an ab-

solute calibration for the optical system, we can obtain $[Cs^+]_e$ (the equilibrium value) from which we then deduce $[Cs^+]_0$ (the value just behind the re-flected shock). We then use $[X^-]_0 = [Cs^+]_0$.

III. THEORY OF MEASUREMENT

The threshold for the absorption of radiation by the negative ion occurs at an energy equal to its elec-tron affinity. This process for the halogen nega-tive ions is written as

$$X^-(^1S_0) + h\nu \rightarrow X(^2P_{3/2,1/2}) + e \ . \tag{4}$$
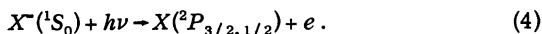
There are thus two absorption thresholds with an energy difference corresponding to the fine-struc-ture splitting of the ground state. For the cases studied here, Cl^- has an absorption edge at 3429 Å $(^2P_{3/2})$ and a second threshold at 3328 Å $(^2P_{1/2})$, and Br^- has an absorption edge at 3685 Å and a second threshold at 3244 Å for these same states, respectively.

The measured absorption signal I is related to the photodetachment cross section σ by the follow-ing equation:

$$\sigma = \frac{\ln(I_0/I)}{[X^-]l} , \tag{5}$$

where I_0 is the uv signal before absorption and l is the optical path length through the shock tube.

The relationship between the measured free-bound radiation and the electron and positive ion densities, which has been derived previously,[8] was used in this work. It has also been shown[8] that the contribution to the measured emission due to neutral bremsstrahlung and Kramers radiation at 4000 Å is small.

IV. EXPERIMENTAL RESULTS

A detailed description of the shock-tube con-struction and operation appears earlier.[8,12] The measurements were made behind the reflected shocks using nitrogen (99.997% pure) purchased from Matheson Corporation and high-purity CsCl and CsBr purchased for Kawecki Chemical Com-pany. Measurements were made between 3700 and 2000 Å for Br^- and between 3500 and 2000 Å for Cl^-.

The measured Br^- photodetachment cross sec-tion as a function of wavelength is shown in Fig. 1, and the measured Cl^- photodetachment cross sec-tion as a function of wavelength is shown in Fig. 2. It should be noted that each experimental point is the average of several measurements.
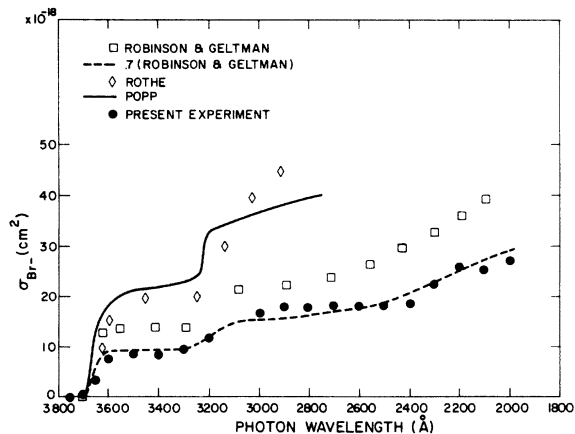

FIG. 1. Photodetachment cross section for Br^-. The dashed line is the calculated cross section of Robinson and Geltman multiplied by 0.7. The data point below the threshold for photodetachment (3750 Å) represents mea-surements which were made to establish that there was no spurious absorption.

V. DISCUSSIONS OF ERRORS AND DATA CORRECTIONS

The absolute value of the measured cross sec-tion hinges on relating the measured X^- absorption to the calibrated $Cs^+ + e$ free-bound emission sig-nal. This is discussed at some length in a pre-vious publication,[8] where we derived an expression for the measured free-bound emission as a func-tion of the temperature, wavelength, free-bound recombination cross section $[\sigma_r(v)]$, and electron
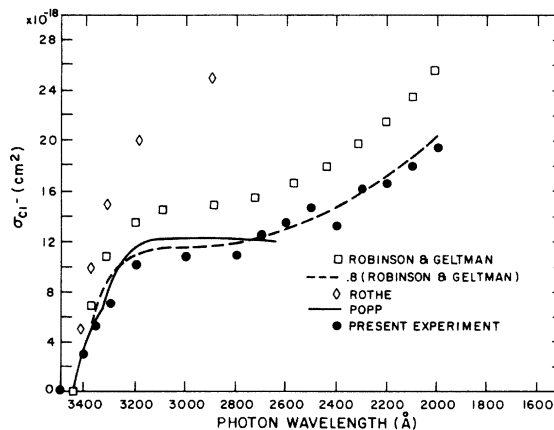

FIG. 2. Photodetachment cross section for Cl^-. The dashed line is the calculated Robinson and Geltman cross section multiplied by 0.8. Again measurements taken below the threshold for photodetachment (3450 Å) estab-lish that no spurious absorption is present.

and ion densities, viz.,

$$I(\lambda) = K[e][Cs^+]v^2\lambda^{-3}T_e^{-3/2}\sigma_r(v)\,\exp\left[\frac{-hc}{kT_e}\left(\frac{1}{\lambda}-\frac{1}{\lambda_0}\right)\right].$$

(6)

By evaluating the effects of both the random and systematic errors on the measured emission signal, as given by Eq. (6), one can assess the effect of these errors in the determination of [Cs⁺]. One source of random error is in the temperature determination. The temperature is determined by measuring the transit time of the incident shock wave as it passes three successive thin-film heat transfer gauges. The transit time is measured to within 1 μsec. This determines the shock speed to better than 0.5%. The temperature is then calculated behind the reflected shock by using the Rankine-Hugoniot relations to calculate the equilibrium temperature. The effect of the seed material (cesium halide salt) was included in the calculations. The random error in the calculated equilibrium temperature is $<\pm 50$ °K. This has an overall effect on the measured emission (Eq. 6) of less than $\pm 1\%$. A somewhat larger source of random error is due to possible density differences along the different geometric paths sampled by the emission and absorption systems which are perpendicular to each other and therefore caused the sampling of different spatial regions of the shock-heated gas. Anisotropic density fluctuations transverse to the shock-tube axis could cause shot-to-shot variations in the measured cross section. We do, in fact, see scatter of $\pm 10\%$, which is to some extent probably due to this effect.

Systematic errors must be corrected for or taken into account in the overall error limits in the cross section. A relatively minor systematic error occurs when one considers the accuracy of the assumption that $[Cs^+]_e = [e]_e$. At our operating temperature equilibrium calculations give $[e]/[Cs^+]$ = 0.987. The accuracy of the absolute radiometry is somewhat more uncertain. As discussed in our previous paper,[8] the radiometer is periodically calibrated using an Eppley calibrated standard tungsten lamp which is double checked periodically with a National Bureau of Standards calibrated optical pyrometer. The lamp and optical pyrometer agreed to within ~3%. Another source of error is the contribution to the measured emission due to neutral bremsstrahlung and Kramers radiation. This varies depending on ion-electron density and neutral-gas density, but is on the order of 1% of the free-bound emission.

Finally, there is an uncertainty of $\pm 15\%$ in the free-bound cross-section values used. These have been both measured[13,14] and calculated[15] with

good agreement (within the expected uncertainties) between theory and experiment. The value of the [Cs⁺] depends only on the square root of the free-bound cross section, however; thus the overall effect of this error is reduced to ~$\pm 8\%$.

When one takes into account all of the above sources of errors, one finds the overall uncertainty in the determined absolute value of the photo-detachment cross section is $\pm 25\%$.

VI. DISCUSSION

Both theoretical calculations and experimental measurements have been included in Fig. 1 and 2. For both Br⁻ and Cl⁻ the results of this experiment are in good agreement with the Robinson and Geltman[1] calculation. The dashed lines (30% below the calculated cross section for Br⁻ and 20% below for Cl⁻) are good fits to our data. Robinson and Geltman claim $\pm 20\%$ accuracy for their calculation, and our measurements are good to within $\pm 25\%$. This indicates good agreement in both absolute magnitude and in the shape of the cross section.

The experimental measurements of Rothe[6] and Popp[7] are each about a factor of 2 above the calculations of Robinson and Geltman for Br⁻, while for Cl⁻ Popp's measurements fall directly on ours, but Rothe's are still about a factor of 2 above calculation. As can be seen from Figs. 1 and 2, our measurements go to much shorter wavelengths than any measurements to date.

Measurements were also made near threshold. Since the resolution of the monochromator was only 32 Å, a precise determination of the threshold wavelength (i.e., electron affinity) could not be made. The electron affinities of these ions are, however, well known, and these measurements are in agreement with the accepted values.[16]

Our previous measurements of F⁻ (Ref. 8) and I⁻ (Ref. 9) photodetachment were also in good agreement with the theoretical work of Robinson and Geltman. The F⁻ values agreed quite well in shape and were about 30% below calculation. The I⁻ cross-section values were in very good agreement down to about 2800 Å. Below 2800 Å we observed what appears to be a resonance. This was not predicted by the Robinson and Geltman calculations, but is described more fully in Ref. 9. The existence of this resonance has recently been confirmed by Nieger.[17]

VII. CONCLUSION

Shock-tube measurements of the photodetachment cross sections of the stable halogen negative ions reported in this paper and previously[8,9] have

been compared with the calculated values of Robin-
son and Geltman.[1] Within the expected uncertain-
ties of both theory and experiment we find good
agreement between the two. These measurements
also were made much further into the uv than any
previous experiments.

ACKNOWLEDGMENT

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