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High-resolution determination of the electron affinity of fluorine and bromine using crossed ion and laser beams

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We report tunable-laser photodetachment of F^- and Br^- ions near the first threshold corresponding to the atomic ${}^2P_{3/2}$ ground state. Using a high-resolution pulsed uv laser calibrated with molecular iodine absorption and doubly crossed laser and ion beam technique, we determine the electron affinities of fluorine and bromine with high accuracy. These determinations account for the hyperfine structure of the atomic ground states of ${}^{19}F$ and ${}^{79}Br$,${}^{81}Br$. The threshold values obtained for the transition between the ion ground state ${}^1S_0$ and the atomic ground hyperfine state ${}^2P_{3/2}$ are 27 432.440(25) cm^{-1} or 3.401 190(4) eV for fluorine and 27 129.170(15) cm^{-1} or 3.363 590(3) eV for bromine, and the isotope shift of Br^-, ${}^{79}Br-{}^{81}Br$ is found to be below our experimental resolution.

INTRODUCTION

Laser-photodetachment spectroscopy of negative ions is the most precise means currently available to measure electron affinities of atoms and molecules. A commonly employed method in making these measurements is laser-photodetachment-threshold (LPT) spectroscopy, whereby one locates directly the threshold for photodetachment from a negative ion (where the detached electron has zero kinetic energy) by sweeping the wavelength of a stabilized narrow-frequency bandwidth laser and observing the characteristic threshold laws of photodetachment from each energy state of the negative ion. With existing laser technology, the experimental resolution of this method is sufficiently high to observe hyperfine structure and even isotope shifts.

Negative ions can be produced in a variety of environments, each environment having distinct experimental advantages and disadvantages. One attractive environment for LPT studies lies in the realm of optogalvanic spectroscopy, by which the electron affinity of iodine has been measured,[1] 3.0591(1) eV [24 673.4(8) cm^{-1}].[2] The virtues of the optogalvanic method are the relative ease of ion production and very simple means of detection. A significant handicap, however, is the extreme disturbance which the ions experience due to the high-pressure plasma environment. This limits the application to just a few negative ions.

Negative ions stored in ion traps is another technique which has shown utility in measuring electron affinities. One such study has produced a high-resolution measurement of the electron affinity of sulfur,[3] 16 752.967(29) cm^{-1}. The sensitivity of ion trap measurements is very high, and the long storage times allow one to probe very weak detachment processes.[4] For certain ions, however, the long storage times allow parasitic chemical processes to systematically alter the signals observed after photodetachment.[5]

A third environment for LPT studies involves a beam of accelerated ions intersecting a laser beam. Ion beams are very attractive because of the ease of production of a variety of negative ions and sensitive detection. It is this implementation of LPT spectroscopy that has resulted in the most precise measurement of an electron affinity, that of oxygen,[6] 11 784.645(6) cm^{-1}. This particular measurement was performed with collinear laser and ion beams with sub-Doppler compression of the velocity spread of the ion beam.[6,7] The simple linear Doppler shifts are canceled from the experimental results by combining the results from parallel and antiparallel beam arrangements.

Ion beam apparatuses of more conventional design, with laser and ion beams crossing at right angle, suffer from the unavoidable Doppler shift resulting from imperfect right-angle intersection of the beams. A solution for this is to employ a second laser-ion beam crossing, i.e., a doubly crossed arrangement, and subsequently combine the photodetachment results to eliminate the linear Doppler shifts. The second-order Doppler shift is usually small but not insignificant. However, it is easily corrected because of its angular independence. The technique of doubly crossed beams involves very minor modifications to existing crossed beams apparatus and should prove to be fruitful for future high-resolution measurements. It is this technique which we have adopted for the present investigation of the electron affinities of fluorine and bromine.

To date, contrary to the case of the Cl^- and I^- ions, there have been no LPT studies undertaken of the ions F^- and Br^-. The current recommended atomic electron affinity[8] of fluorine is 3.399(3) eV, and for bromine it is 3.365(3) eV. In this paper we report more precise values of these electron affinites, improving the precision by three orders of magnitude.

EXPERIMENTAL TECHNIQUE

Two primary features of the experimental setup, the ion beam and the laser system, have been described in previous publications.[9,10] The ion beam runs at 1.2 keV with a current of 20–50 nA, and the beam is collimated in the interaction region by means of electrostatic optics and diaphragms. There are, in fact, two interaction regions spatially displaced from one another where the ion beam intersects, at nearly normal incidence, two parallel laser beams which propagate in opposite directions. The two interaction regions thus have equal and opposite linear Doppler shifts. Beyond the interaction region the continuous current of undetached ions is electrostatically deviated into a Faraday cup, and the neutral atoms created by photodetachment are detected, by virtue of their kinetic energy, with an electron multiplier.

The uv radiation at 365 nm is obtained by frequency doubling a pulsed single-mode dye laser operating at 730 nm. We use a single cavity injection system with a dye jet pumped by a cw argon-ion laser and an intracavity dye cell, which is pumped by a small portion of the green second harmonic of a Nd:YAG (yttrium aluminum garnet) laser. The resulting radiation pulses have nearly the same spectral and spatial quality as the cw radiation. The pulses are next amplified in three external dye cells which are pumped by the remaining green light of the YAG laser. Finally, the pulses are frequency doubled by a KDP crystal and the uv is separated from the red fundamental beam by a dichroic reflector. The pulsed uv radiation has a repetition rate of 10 Hz, a duration of 10 ns, a peak power of 1 MW, and a bandwidth of 80 MHz. Frequency scanning and stabilizing the laser system is achieved by servolocking the ring cavity to a sigmameter.[11] The continuous tuning range of the uv is about 100 GHz.

The photon energy of the red laser is measured in two steps: first, a rough estimate is made by means of a spectroscope (error equal to 0.5 cm^{-1}), then an absolute energy measurement is made by locating various molecular iodine absorption lines,[12] which are known with a total uncertainty lower than 0.005 cm^{-1}. To this end, a part of the laser beam passes through a 30-cm-long hot-wall iodine cell which is heated to 500 °C and which has a cooled finger at the temperature of 60 °C. The light beam transmitted through the iodine cell and a reference beam passing outside the cell are measured by two photodiodes, and the photocurrents are subtracted, effectively eliminating laser amplitude noise from the calibration.

The large values of the ion velocity (110.0 km/s for F^-, 53.95 km/s for $^{79}\text{Br}^-$, and 53.27 km/s for $^{81}\text{Br}^-$) require strict right-angle crossing of the ion and laser beams in order to eliminate the linear Doppler shift. The practical difficulty of fulfilling such a condition leads us to employ a second crossing, spatially separate from the first one, using a corner cube reflector. Under these conditions, photodetachment from the parallel incident and reflected beams can both be recorded in order to account for a residual error in the crossing angle. To avoid Doppler broadening due to a convergent or divergent laser beam in the interaction region, the laser system is constrained to operate in the TEM_{00} mode, and the beam is imaged to quasiplanar wave fronts with a spot diameter of 0.5–1.0 cm in the two interaction regions. The light intensity is limited in order to avoid saturating the photodetachment and to avoid light shifts. Moreover, the transit time of the ions through each interaction region is larger than the laser pulse time width, which results in negligible spectral broadening (≤ 1 MHz).

Figure 1 shows an oscilloscope display of the time behavior of the detachment signals for an ion beam of natural bromine in which the two stable isotopes $^{79}\text{Br}^-$ and $^{81}\text{Br}^-$ are both apparent. Owing to the flight length between the two interaction regions, it is possible to temporally separate the photodetachment signals from each beam crossing. Furthermore, because of the distance between interaction regions and the detector, and of the different velocities of the isotopes, the two natural isotopes of bromine are separately detected. For bromine, one sees four peaks in the oscilloscope trace, i.e., two crossings each for two isotopes. As there is only a single stable isotope in natural fluorine, ^{19}F, only two peaks appear for F^- corresponding to the separate beam crossings.

A Gould digital oscilloscope interfaced to a minicomputer (PDP11/23) performs the data acquisition and storage. The photodetachment response signal and a normalization signal of the uv intensity are entered into two channels of the oscilloscope at the 10-Hz laser repetition rate. The sampling proceeds with 10-ns duration steps, digitization, and averaging over 16 laser shots. The area under each peak in the photodetachment response is recorded along with the calibration signal of the I_2 photoabsorption which is digitized by an analog-digital converter. The data analysis is performed off line with a personal computer.

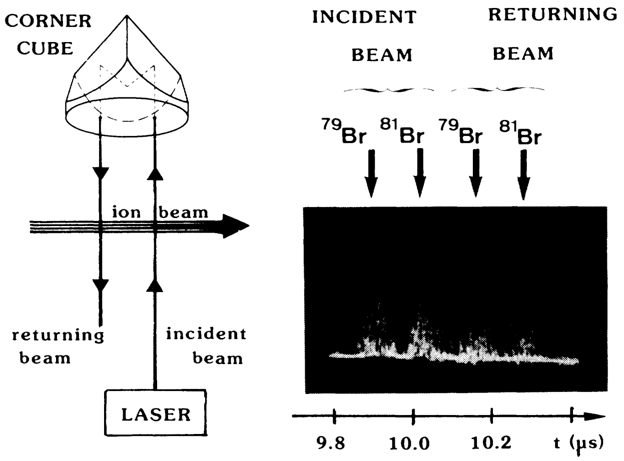

FIG. 1. Scheme of the optical setup and the interaction regions showing the two ion and laser beam crossings, and an oscilloscope trace of the detachment signals from a Br^- ion beam. The positions of the packets of neutral atoms produced by the photodetachment give the time of flight from the crossings to the electron multiplier. The origin of the time scale is the trigger from the laser pulse, and the delay is about 125 ns between the two bromine isotopes, and 260 ns between the two crossings (separated by 1.4 cm).

DATA ANALYSIS, RESULTS, AND DISCUSSION

A photodetached electron extracted from a p orbital must change its parity to even, thus the detached electron wave must be either an s or d wave. For a small energy range above the $^2P_{3/2}$ threshold, the d wave is suppressed by the centrifugal barrier, and its cross section is negligible compared to that of the s partial wave up to several hundred wave numbers. The Wigner threshold law[13] for s-wave detachment takes the form $\sigma(E)\propto(E-E_{\text{th}})^{1/2}$ where E is the photon energy and E_{th} is the threshold energy. The only complication arising is the presence of hyperfine structure in the neutral atom's ground state, which is ordinarily neglected because of its absence or its smallness compared to the experimental resolution ($\simeq 0.1$ cm^{-1}). In the present investigation, however, we find it necessary to account for the hyperfine thresholds E_F; there being two hyperfine states in the case of ^{19}F ($I=\frac{1}{2}$; $F=1,2$) and four in the case of bromine with each isotope having similar hyperfine structure, ^{79}Br and ^{81}Br ($I=\frac{3}{2}$; $F=0,1,2,3$). The values of the hyperfine separations are known,[14] and since the ground state of the negative ion is a nondegenerate $^1S_0$, the hyperfine thresholds are weighted only according to the degeneracy of the final state of the neutral halogen. The partial cross section for detachment to a particular hyperfine state is thus

$$\sigma(E,F)=K(2F+1)(E-E_F)^{1/2}, \quad E\geq E_F$$

$$\sigma(E,F)=0, \quad E\leq E_F$$

where E_F is the threshold energy for detachment to the F hyperfine state of the neutral halogen, and K is a constant. The total detachment cross section is simply the sum of the partial cross sections:

$$\sigma(E)=\sum_F \sigma(E,F) \ .$$

To account for finite experimental resolution, the cross section is convolved with a Gaussian function which phenomenologically represents the residual Doppler broadening and laser linewidth. We perform a least-squares fit of the data to this model and derive the threshold energy for the hyperfine states of lowest F ($F=1$ for fluorine and $F=0$ for bromine). An example of photodetachment data and a fit to the detachment model are shown in Fig. 2. Also shown in this figure are the iodine spectrum and the result of the calibration fit. In these data, the frequency range scanned by the pulsed uv laser is 80 GHz, i.e., twice the range shown in the iodine spectrum. Since the iodine is irradiated with the red laser output and the ions with the frequency doubled light, the absorption lines of the iodine fix the absolute calibration of the photodetachment spectrum after doubling the energies shown in the iodine spectra.

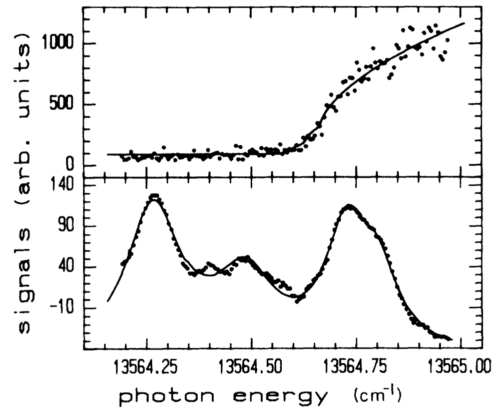

FIG. 2. Photodetachment spectrum of ^{79}Br$^-$ to the $^2P_{3/2}$ threshold and the results of a fit to a photodetachment model including the hyperfine structure of the final state of the atom (above). Also shown (below) is the iodine calibration spectrum. The wave-number scale should be doubled in order to interpret the photodetachment spectrum.

The value of the electron affinity can be determined by combining the threshold values obtained from the two crossings in order to eliminate the opposite linear Doppler shifts. The threshold value is

$$\nu_{\text{th}}=\tfrac{1}{2}(\nu_i+\nu_r)[1-(v/c)^2]^{-1/2} \ ,$$

where ν_i and ν_r are the measured laser frequencies for the detachment thresholds of the incident and returning laser beams (i.e., first and second crossings). After performing least-squares fits on the data and extracting threshold values for each crossing, we combine the values for the two crossings to eliminate the linear Doppler shift. Each experimental assay thus results in a corrected threshold value. We then perform a weighted average of the results using the propagated statistical errors of the threshold parameters as the weights. We obtain finally the electron affinity for fluorine, $\mathcal{E}_{\text{EA}}(\text{F})=27\,432.440(25)$ cm^{-1}, and for bromine $\mathcal{E}_{\text{EA}}(\text{Br})=27\,129.170(15)$ cm^{-1}. These values are consistent with previous determinations[8,15] and are more precise. The errors quoted here are approximately three times the statistical errors from the fits as propagated through the procedure for the weighted averages.

The isotopic shift of bromine is found to be smaller than our experimental resolution. It is possible, nevertheless, to locate its value within the limits $|\mathcal{E}_{\text{EA}}(^{81}\text{Br})-\mathcal{E}_{\text{EA}}(^{79}\text{Br})|<300$ MHz. As a point of comparison, the normal mass shift is roughly 140 MHz. Calculations of a specific mass shift and of the volume isotope shift are beyond the scope of this paper.[16]

CONCLUSION

We have presented an efficient experimental method for determining electron affinities with high precision.

The application to fluorine and bromine yields new values of their electron affinities given with relative uncertainties of better than 1×10^{-6}, which are considerably better than previous results. Further measurements are in preparation on two-photon near-threshold detachment of the fluorine and bromine negative ions. These results will be compared with those obtained in a recent experiment of two-photon detachment from the negative chlorine ion[5] which found that the order of nonlinearity of the detachment significantly deviated from the prediction of lowest-order perturbation theory.

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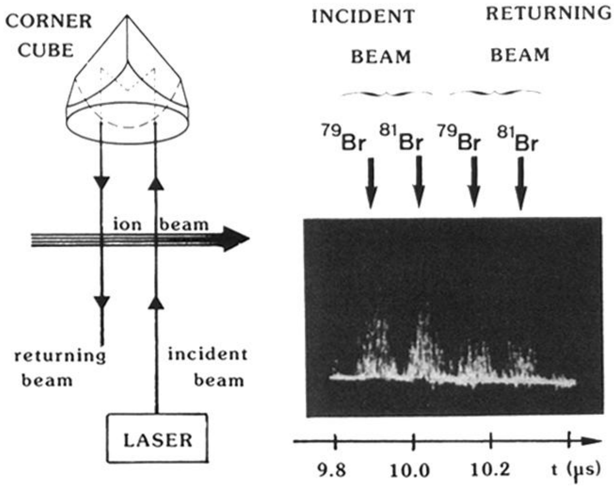

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