Photodetachment studies with the linear time of flight photoelectron spectrometer

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Abstract. A linear time of flight photoelectron spectrometer was built for photodetachment studies on anions. The design of the newly constructed photoelectron spectrometer is discussed briefly. Angular distribution of photoelectrons in the photodetachment from $\text{OH}^-$, $\text{As}^-$ and $\text{Cu}^-$ were measured at a few distinct wavelengths. Energy dependence of the asymmetry parameter was studied for these anions. The relation between electronic configuration and the energy dependence of the asymmetry parameter is briefly discussed.

1. Introduction
Negative ions play a vital role in a variety of phenomena that occur in plasmas, earth’s atmosphere, surface dynamics and in many other fields [1]. They play a key role in understanding the emission spectra of celestial objects which are interestingly influenced by their anion atmosphere [2]. All the atomic anions except $\text{H}^-$ are bound by short range interaction between the neutral core and the “extra” electron. This short - range interaction accounts for most of the interesting properties in anions and these in turn provide an excellent opportunity to understand the structure and dynamics of systems with such short range interactions. The structure and binding energy of anions are largely determined by the electron – electron interactions and hence the experimental studies on anions critically evaluate various theoretical models that account for electron correlations [7]. Advanced laser techniques [3], efficient anion sources [1], storage rings [4], synchrotron sources [5] and advanced imaging techniques [6] have been steadily extending the frontiers in the negative ion research in the recent years.

Photodetachment experiment in which the “extra” electron in the anion is detached to the continuum by the absorption of photon(s) of appropriate energy has been extensively employed in probing various aspects in the negative ion research. Photodetachment studies help in understanding the dynamics of the excited electronic states and can provide complementary information to that obtained in Dissociative Electron Attachment experiments [8]. Conventional spectroscopy of neutral species has limitations determined by the forbidden transitions and the availability of longer wavelength laser with sufficient intensity to access levels too close to the ground electronic state. Photoelectron spectroscopy of the corresponding anion is an elegant technique in overcoming these problems and has been extensively employed for spectroscopic studies on neutral species [9]. Photodetachment experiments employ specialized forms such as Laser Photodetachment Threshold technique (LPT) [10], Laser Photodetachment Electron Spectrometry (LPES) [11], Tunable IR Laser Photodetachment spectroscopy [12], Threshold studies with resonance ionization detection [13].
Resonant multiphoton detachment [14], Stimulated Raman scattering detachment spectroscopy [15], Laser photodetachment microscopy [16] and accelerator mass spectrometry [17] etc.

Apart from the kinetic energy measurements, the angular distribution of photoelectrons provides critical data on the photodetachment process. These measurements have been done using conventional techniques by changing the laser polarization direction or a turn-table technique. More recently Velocity Map Imaging (VMI) has been used for obtaining the angular distribution data along with photoelectron kinetic energy spectra [6].

Measurement of the differential cross sections for photodetachment process is very important for structural studies on anions. Angular distributions yield the relative strength of the transition amplitudes involved in the photodetachment process and the relative phases between them. The differential cross section for single photon detachment of an unpolarized target, under electric dipole approximation, can be described as

\[
\frac{d\sigma}{d\Omega} = \left(\frac{\sigma}{4\pi}\right)\left[1 + \beta \left(3\cos^2\theta - 1\right)\right].
\]

where \(\sigma\) and \(\beta\) are the total photodetachment cross section and the anisotropy parameter, respectively. The anisotropy parameter has all the information about the dynamics relevant to the angular distribution of photoelectrons. The spectral dependence of \(\beta\) is characteristic of the anion and is important in the study of structure and dynamics of the anions. Spectral dependence of anisotropy parameter show pronounced variation near autoionizing resonances due to enhancement of weak relativistic and spin orbit interactions [19]. Measurement of anisotropy parameter near autodetaching resonance would provide excellent opportunity to study these weak effects that remain overshadowed in the direct detachment process.

We have built a photodetachment experiment using a linear time of flight photoelectron spectrometer [18] and have used it to study the photoelectron angular distribution for a few anions like \(\text{OH}^-\), \(\text{Cu}^-\) and \(\text{As}^-\). The motivations behind these measurements were to study the dependence of the anisotropy parameter on the photoelectron energy and the influence of electronic configuration on such energy dependence of the anisotropy parameter.

2. Experimental Method

Figure 1 shows the schematic for the experimental setup. Negative ions were produced using Cesium sputter source [20]. The ion source was operated at 1 – 2 KV cathode voltage. The sputtered negative ions were extracted and accelerated to about 3 KeV. The ion source was maintained at about \(1 \times 10^{-7}\) Torr vacuum using a diffusion pump. The accelerated ion beam is transported to the Wein filter region using deflectors and two sets of Einzel lens. The mass analyzed ion beam was focused on to the interaction region using a third Einzel lens. The total ion beam path was about 1.5 m. The ion beam current was monitored throughout the measurements using a Faraday cup in the post interaction region. The interaction region was maintained at a high vacuum of about \(2 \times 10^{-8}\) Torr using a turbo molecular pump backed by an oil free pump. The interaction region was differentially isolated from the ion source region. This was done to keep the interaction region clean thereby minimizing the background electrons produced by collisional detachment as well as possible multi photon ionization of large background molecules. The interaction chamber was a six way cross of 6 inch diameter made out of non-magnetic stainless steel. The laser beam and the ion beam intersected at right angles at the centre of the interaction chamber. A linear time of flight photoelectron spectrometer of 1 m length and 5 cm in diameter mounted over the interaction chamber was used to collect the photoelectrons in the direction perpendicular to the plane containing the two beams. The entrance to the flight tube had an aperture of 3.5mm diameter and was 2.5 cm away from the point of intersection of the two beams. This aperture defined the angular resolution of the measurements to \(6^\circ\), after taking into account the finite size of the interaction region. The electrons were detected at the end of the flight tube by a pair
of Micro Channel Plate (MCP) electron detectors of 40 mm active diameter arranged in the chevron configuration. The detector end of the flight tube was pumped by a turbo molecular pump to a vacuum of about $2 \times 10^{-8}$ Torr vacuum.

Figure 1. Schematic diagram of the anion photodetachment experimental arrangement showing the sputter ion source, ion-optics system, Wein’s Mass filter, linear time of flight photoelectron spectrometer and the laser system.

Low energy electron detection needs minimization of stray electric and magnetic fields which would otherwise deflect away the electrons before they can reach the detector. The interaction chamber and all parts in the linear TOF assembly were completely built with non-magnetic materials. The interaction chamber and the flight tube were electropolished to maintain good surface properties. The photoelectron spectrometer was shielded from earth’s magnetic field by wrapping two magnetically isolated layers of $\mu$ metal sheets. The interaction region and the flight tube have two separate $\mu$ metal shielding as shown in the schematic diagram. The $\mu$ metal sheets in the interaction chamber were hydrogen annealed after rolling into cylindrical form thereby reducing the field inside to $\sim 7$ mG. This region was thus essentially field free and only those electrons that enter the 3.5 mm diameter aperture in the flight tube were allowed to enter the flight tube. Since the $\mu$ metal shielding outside the flight tube could not be hydrogen annealed, the magnetic shielding was not satisfactory along the flight tube. This resulted in poor transmission of electrons. This problem was solved by having a solenoid wound around the flight tube, but inside the $\mu$ metal shield. A weak magnetic field of about 0.4 Gauss produced by this solenoid along the flight tube was found to be sufficient to guide the electrons up to the detector, without sacrificing the angular resolution.

The photon beams used in these experiments were produced using Excimer pumped Dye Laser, a custom made Nd:YAG laser of 100 Hz repetition rate and an Nd:YAG pumped dye laser. The dyes used for the measurements on As$^-$ were Rhodamine 6G (565nm), Rhodamine 101(603nm), DCM (637nm) and Pyridine (698nm and 715 nm). The dyes used for the measurements on OH$^-$ were Coumarin 2 (440nm) and Stilbene 3 (400 nm). The laser output was about 4 mJ and 15ns in pulse width. The output power of the laser was monitored and was employed for normalization. The laser
beam was polarized using a Glan Thompson polarizing prism with an extinction ratio ~ $10^{-5}$. The laser polarization was rotated, with respect to the electron collection direction, using a double Fresnel rhomb.

The negative ion beam passed through two guiding apertures of about 4mm x 1.5mm size, separated by 5 cm. The slits were placed 6 cm upstream of the interaction region. The laser beam was aligned to maximize the photoelectron signal. Extreme care was taken while aligning the laser to minimize the laser "walk through" to less than 0.1mm during rotation of the double Fresnel rhomb. This was needed to avoid variation of the laser - ion overlap throughout the angular distribution measurement. The laser beam size at the interaction region was about 3mm in diameter.

3. Results and Discussion

The experimental apparatus and the measurement procedure were tested by measuring the angular distribution for Cu$^-$($^1S_0 + h\nu \rightarrow ^2S_{1/2} + e^-$) for which the angular distribution is known to peak along the laser polarization. Rotation of the double Fresnel Rhomb by $\theta$ results in the rotation of the linear polarization of the laser by $2\theta$. At each of wavelength under consideration, the photoelectron spectra were taken by rotating the double Fresnel rhomb in steps of $8^\circ$. The resolution of the photoelectron spectrometer was about 50 meV at 1 eV. The photoelectron yield was taken to be the area under the photoelectron spectra. The normalized yield of photoelectron, at various laser polarization angles $\theta$, were least squared fitted to $Y(\theta) = a[1+ \beta P_2[\cos(\alpha-\phi)]$, where $P_2[\cos(\theta)]$ is the second order Legendre polynomial, $\alpha$ is the dial reading on the Double Fresnel Rhomb mount, $a$, $\alpha$ and $\beta$ are parameters in the least square fit. The angular resolution of our spectrometer is about $6^\circ$ and is determined by the aperture in the interaction side end of the flight tube as mentioned earlier. The finite angular resolution, which was mentioned previously, was taken into account during the least square fitting procedure. Figure 2 gives the angular distribution for Cu$^-$($^1S_0 + h\nu \rightarrow ^2S_{1/2} + e^-$) at 355 nm. Table 1 gives the measured anisotropy parameter for Cu$^-$($^1S_0 + h\nu \rightarrow ^2S_{1/2} + e^-$) at three wavelengths. The measured anisotropy parameters were energy independent with a value equal to 2, as expected [21], thus confirming the reliability of our measurements.

![Figure 2](image_url)

**Figure 2.** Angular distribution for Cu$^-$($^1S_0 + h\nu \rightarrow ^2S_{1/2} + e^-$) photodetachment process at 355nm. The normalized photoelectron yield was recorded while rotating the double Fresnel rhomb in steps of $8^\circ$. The measured normalized yield was then least square fitted to $Y(\theta) = a[1+ \beta P_2[\cos(\alpha-\phi)]$ and the fit is shown as the solid line. The error bars for the normalized yield are to one standard deviation and those for the angle represent $6^\circ$ angular resolution in our measurements.

| Wavelength (nm) | Photoelectron energy (eV) | Anisotropy parameter ($\beta$) |
|---------------|---------------------------|-----------------------------|
| 532           | 1.09                      | 1.98 ± 0.10                 |
| 355           | 2.25                      | 1.95 ± 0.10                 |
| 266           | 3.38                      | 1.95 ± 0.06                 |

Table 1 Measured anisotropy parameters for Cu$^-$($^1S_0 + h\nu \rightarrow ^2S_{1/2} + e^-$) photodetachment process at 532nm, 355nm and 266nm.
The photoelectron spectra were recorded at four different laser wavelengths of 266 nm, 355 nm, 400 nm and 440 nm for the transition, \( \text{OH}^- (\Sigma^+ \leftarrow \chi) + h\nu \rightarrow \text{OH} (\Pi) + e^- \). Figure 3 shows the typical photoelectron spectrum for OH\(^-\) at 355 nm. Figure 4 gives the measured photoelectron angular distribution for OH\(^-\) at 440 nm. Table 2 gives the measured anisotropy parameter for the photodetachment of OH\(^-\) anion at four different wavelengths. The measurements clearly show energy dependence of the anisotropy parameter for the OH\(^-\) photodetachment.

![Figure 3. Photoelectron spectrum for OH\(^-\) at 355nm.](image)

![Figure 4. Angular distribution for OH\(^-\) at 440nm.](image)
Table 2. Measured anisotropy parameters for OH- ($\left( ^1\Sigma^+ \right) + h\nu \rightarrow OH \left( ^3\Pi \right) + e^{-}$) photodetachment process

| Wavelength (nm) | Photoelectron Energy (eV) | Anisotropy parameter (\(\beta\)) |
|-----------------|---------------------------|----------------------------------|
| 266             | 2.78                      | -0.22 ± 0.02                     |
| 355             | 1.65                      | -0.72 ± 0.03                     |
| 400             | 1.22                      | -0.78 ± 0.03                     |
| 440             | 0.98                      | -0.90 ± 0.03                     |

Survey of previous studies on spectral dependence of the anisotropy parameter motivates to investigate the influence of electronic configuration on the spectral dependence of anisotropy parameter. Anions of Group IV [22] show similarity in the spectral dependence of the anisotropy parameter whereas the B\(^-\) [23] and Al\(^-\) [24] show marked dissimilarity in the spectral dependence of their anisotropy parameters. It is therefore necessary to study a larger set of isoelectronic anions to understand the influence of the electronic configuration on the spectral dependence of the anisotropy parameter. P\(^-\) [24] is the only anion of Group V elements that was previously studied. We studied the photodetachment of As\(^-\), which is isoelectronic with P\(^-\). Figure 5 shows the photoelectron spectrum for As\(^-\) photodetachment process at 698 nm. The ground state of the As\(^-\) is \(^3P\) and that of As is \(^4S_{3/2}\). The fine structure splitting for this state is known to be \((^3P_2 \rightarrow ^3P_1) = 1008 \text{ cm}^{-1}\) and \((^3P_2 \rightarrow ^3P_0) = 1339 \text{ cm}^{-1}\) [25]. The ion source operated at the conditions mentioned earlier yielded predominantly \(^3P_2\), while weakly populating \(^3P_1\) and \(^3P_0\). The transitions \((^3P_1 \rightarrow ^4S_{3/2})\) and \((^3P_0 \rightarrow ^4S_{3/2})\) were much too weak for good statistics. We studied the angular distribution for As\(^-\) \((^3P_2 \rightarrow ^4S_{3/2})\) transition, which defines the electron affinity of As\(^-\). The photoelectron angular distribution was measured at six different wavelengths. Figure 6 shows the measured angular distribution at 698 nm. The anisotropy parameters determined from the measured angular distributions are given in Table 3. The results show energy dependence of the anisotropy parameter for the As\(^-\) photodetachment process.

Figure 5. Photoelectron spectrum for As\(^-\) \((^3P_2 + h\nu \rightarrow ^4S_{3/2} + e^{-})\) photodetachment process at 698 nm.
Figure 6. Angular distribution for As\(^{−}\)\((^{3}P_{2} + h\nu \rightarrow ^{4}S_{3/2} + e^{−}\) process at 698 nm. The normalized photoelectron yield was recorded while rotating the double Fresnel rhomb in steps of 6°. The measured normalized yield was then least square fitted to \(Y(\theta) = a[1 + \beta P_{2} \cos(\alpha - \phi)]\) and the fit is shown as the solid line. The error bars for the normalized yield are to one standard deviation and those for the angle represent 6° angular resolution in our measurements.

Table 3. Measured asymmetry parameters for As\(^{−}\)\((^{3}P_{2} + h\nu \rightarrow ^{4}S_{3/2} + e^{−}\) photodetachment process at six different wavelengths

| Wavelength (nm) | Photoelectron Energy (eV) | Anisotropy parameter (\(\beta\)) |
|----------------|---------------------------|---------------------------------|
| 532           | 1.5                       | -0.23 ± 0.02                    |
| 565           | 1.36                      | -0.33 ± 0.03                    |
| 603           | 1.23                      | -0.39 ± 0.02                    |
| 637           | 1.12                      | -0.52 ± 0.04                    |
| 698           | 0.95                      | -0.58 ± 0.03                    |
| 715           | 0.9                       | -0.58 ± 0.07                    |

To the best of our knowledge there is no explicit calculation for the anisotropy parameter for As\(^{−}\) photodetachment. However, the measured anisotropy parameter for As\(^{−}\) photodetachment is fitted to a simplified form of Cooper-Zare model [26, 27]. In this model the anisotropy parameter as a function of photoelectron energy \(\epsilon\) is given by

\[
\beta(\epsilon) = \frac{2A_{2}\epsilon(A_{2}\epsilon - 2c)}{1 + 2A_{2}^{2}\epsilon^{2}}
\]  

(2)

Where \(\epsilon\) is the photoelectron kinetic energy, \(A_{2}\) is the relative size of the two matrix elements involved in the photodetachment process and \(c\) is cosine of the relative phase between the matrix elements. Figure 7 shows fit of the measured asymmetry parameters to this model. The values for the parameters of the least square fit are \(A_{2} = 0.76\) eV\(^{-1}\) and \(c = 0.77\). Figure 7 also shows the fit for the previously studied anisotropy parameters for P\(^{−}\) photodetachment with \(A_{2} = 0.94\) eV\(^{-1}\) and \(c = 0.75\). The values for the relative phase for these two anions of Group V are nearly same. The difference in the value of \(A_{2}\) for As\(^{−}\) and P\(^{−}\) is due to the different initial and final state radial dipole matrices. The similarity in the relative phases can be attributed to same term quantum numbers for the initial and final state for both these anions. Such a similarity was previously observed among anions of Group IV elements [22]. Though anions of Group IV and Group V both have same orbital angular momentum for the detaching electron and the outgoing partial waves, their relative phases differ because of
different term quantum numbers for the initial and final states. This dependence of the relative phase on the term quantum numbers indicates the anisotropic nature of the neutral residue – detached electron interactions. Further the dependence of the physical parameters of the photodetachment process, such as the relative phase, on the anion electronic configuration should aid in understanding the electron correlations in anions.

Figure 7. The filled circles represent the measured asymmetry parameters for As\(^{-} (1P_2 + h\nu \rightarrow 3S_{3/2} + e^-)\) photo detachment at six different wavelengths. The asymmetry parameters were determined from the measured angular distributions. The solid line represents the fit of the measured asymmetry parameters to the simplified form of the Cooper Zare model. The values for the fit parameters are \(A_2 = 0.76\ eV^{-1}\) and \(c = 0.77\). The filled triangles are the previously reported asymmetry parameters for the photodetachment of P\(^-\) and the dashed line represents its fit to the same model. The values for the fit parameters in P\(^-\) photodetachment are \(A_2 = 0.94\ eV^{-1}\) and \(c = 0.75\).

4. Summary
The design of the newly constructed linear time of flight photoelectron spectrometer is discussed briefly. Photoelectron angular distributions in the photodetachment from Cu\(^-\), OH\(^-\) and As\(^-\) were measured at discrete photon wavelengths. Measurements show energy dependence of the anisotropy parameter for OH\(^-\) and As\(^-\) and energy independence, as expected, of the anisotropy parameter in the case of Cu\(^-\). The anisotropy parameters determined from the measured angular distribution for As\(^-\) is fit to a simplified form of the Cooper – Zare model. The data on Group IV and Group V anions show similarity in the relative phase value among isoelectronic anions. The relative phase values for Group IV (\(c \sim 0.9\)) and Group V (\(c \sim 0.75\)) differ due to their different initial and final state term quantum numbers. The “term – dependence” of the relative phase indicates the anisotropic nature of the interaction between the detached electron and the neutral residue. Physical parameters of the photodetachment process that are determined by the electronic configuration should aid in understanding the electron correlations in anions. We believe that this work would encourage theoretical investigations of the photodetachment of As\(^-\) and OH\(^-\).

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