Photodetachment of O⁻ from threshold to 1.2 eV electron kinetic energy using Velocity-Map Imaging

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Abstract: High-resolution photoelectron imaging from O⁻ with excess energies between 0.5 meV and 1.2 eV is reported. With electron energy resolutions ranging from 266 µeV to 3 meV, branching ratios and angular-distribution asymmetry parameters for each of the fine-structure transitions were measured. Preliminary data for a subset of these measurements showing possible effects due to electron correlation at low excess energy are presented, in the hope of stimulating further theoretical calculations for this species.

1. Introduction
Photodetachment experiments not only provide valuable data on negative ions relevant to fields such as astrophysics, atmospheric and plasma physics and chemistry, but they also provide the ideal environment to study electron-correlation effects. This is due to the lack of a long-range nuclear Coulombic attraction potential, \( \propto r^{-1} \), with the electron instead being bound by a short-range potential of the order \( r^{-4} \). Because of this, subtle electron-correlation and relativistic effects can be studied via photodetachment without being overwhelmed by the strong long-range nuclear Coulombic potential, as is the case in photoionization [1]. Despite this unique environment, experimental photodetachment data, especially angular distributions, are limited in number compared with the situation for photoionization.

To date, most of the measurements undertaken on negative ions have focused on determining cross sections and/or the electron affinity (EA), with only a few measurements additionally determining the photoelectron angular dependence at some finite electron kinetic energy (eKE) [1,2]. Non-threshold photodetachment measurements have been limited to photoelectrons with eKEs from 100’s meV to 10’s eV. At these eKEs the interaction time of the outgoing electrons with the neutral target is small and any structure (within cross sections or angular distributions) resulting from correlation effects is usually small and overwhelmed by experimental uncertainties, unless near a resonance. Lowering of the eKE increases the interaction time, allowing for an enhancement of the electron correlation effects and the resulting structure.

Velocity-map imaging (VMI) is proving to be a very versatile technique, capable of being used to determine photoelectron spectra and their full angular distributions simultaneously, allowing the extraction of angular-distribution asymmetry parameters, branching ratios and cross sections. VMI also offers the unique ability to map electrons with moderate to very low eKEs while maintaining resolving power, thus increasing the absolute photoelectron energy resolution, with near unity collection efficiency. This latter feature helps to mitigate the dramatic loss of photoelectron signal due to the very small magnitude of cross sections at threshold. However, until recently the relative energy resolutions reported using VMI have been limited to \( \Delta E/E \geq 2.0\% \) [3]. With this level of resolution, features such as the fine-structure levels of light atoms, molecular rotational levels and even some vibrational features cannot be resolved.

In 2007, we reported a dramatic improvement in the resolving power of a VMI apparatus [3] achieving a \( \Delta E/E = 0.38\% \) (\( \Delta v/v = 0.19\% \)) for eKE \( \approx 1 \) eV. This was not only significant in terms of...
the resolving power achievable with a VMI spectrometer, but it has allowed the measurement of photoelectron spectra and angular distributions, simultaneously, for light atoms where fine-structure transitions are resolved at eKEs well away from threshold.

In this paper, preliminary results for the photodetachment of O⁻ are presented. When photodetaching O⁻ below a photon energy of 3 eV six fine-structure transitions are accessible,

\[ \text{O}^-\left( ^2P_{3/2,1/2}\right) + \text{hv} \rightarrow \text{O}\left( ^2P_{2,1,0}\right) + \text{e}^-, \]  

where the subscripts refer to the total angular momentum \( J \). The data shown includes photoelectron spectra and angular distributions for eKEs between 500 \( \mu \)eV and 1.2 eV, with electron energy resolutions from 200 \( \mu \)eV to several meV. Also presented is the photoelectron branching ratio between two transitions originating from the ground state of the ion, and a detailed plot of the angular-distribution asymmetry parameter for the sub-transition defining the electron affinity. Recently Garand et al. [4] claimed a somewhat higher resolution than that reported in our publication [3]. This claim is not directly comparable as their reported resolution was achieved at a much longer wavelength than in our publication where the eKEs were 30 – 90 times higher. For a direct comparison of electron energy resolution the values reported in this publication are more relevant.

2. Experimental

The fast anion beam VMI spectrometer has been described elsewhere [3], therefore only a limited description will be given here. The experimental apparatus used in this work (shown in Fig. 1), produces a collimated beam of mass-selected negative ions, which are then interrogated by a laser beam, producing photoelectrons. The detached photoelectrons are imaged using a VMI lens and a multichannel-plate phosphor detector where the photo events are captured with a CMOS camera and each frame is analysed by a PC.

![Figure 1](image-url)  

**Figure 1.** A schematic of the fast anion-beam VMI spectrometer, highlighting its three main regions: Source region (1-5): pulsed ion source and initial acceleration optics; Time-of-Flight (TOF) region (6-10): mass TOF containing ion optics; Imaging region (11-14): VMI spectrometer, MCP/phosphor detector and CMOS camera.

The VMI lens was designed to accommodate a fast ion beam with beam energies from 100’s eV to keV and an interaction-region volume of at least 2 mm³, while achieving high resolution (\( \Delta E/E \approx 0.3\% \)). Imaging of the photoelectrons is performed using a pair of high dynamic-range image-quality 10 \( \mu \)m-pore microchannel plates (MCPs), a P47 phosphor screen and a 4.2 Mega pixel (2048 × 2048) monochrome Peltier-cooled CMOS camera (PCO AG, PCO2000).

Photoelectrons are produced by crossing the ion beam with a detachment-laser beam generated by a Continuum Sunlite EX optical parametric oscillator (OPO) pumped by a Continuum Powerlite 9010 Nd:YAG laser operated at its third harmonic, 355 nm. For the presented measurements the OPO was operated at 10 Hz with pulse energies in the range of 1 mJ – 3 mJ. Given that the measurements were conducted at a series of wavelengths, the output wavelength of the OPO was measured using a high quality wavemeter (HighFinesse, WS7-UV).
For extraction of the 3D photoelectron distribution from the 2D velocity-map image, an inverse Abel transformation was used, as described by Hansen and Law [5]. Before extraction of the 3D photoelectron distribution, small distortions in the image, resulting mainly from the optical lens system coupling the phosphor to the camera, were removed using a circularisation procedure outlined in [3].

As with all VMI spectrometers, the resolving power of our instrument is maintained for all eKEs, as well as the collection efficiency of the lens itself. With eKEs of 1 eV, instrumental resolving powers of $\Delta E/E = 0.38\%$ are easily obtained, resulting in absolute electron energy resolutions of $2 - 3$ meV, full-width at half maximum (FWHM). When operated with eKEs < 100 meV, the absolute electron energy resolution is improved substantially, and for our spectrometer $\mu$eV resolutions are obtained. For all measurements, the laser electric-field vector is in the vertical direction, parallel to the MCPs.

3. Results and Discussion

Figure 2 shows a velocity-mapped image (inset) and the corresponding photoelectron spectrum taken at a wavelength corresponding to conditions close to threshold, 832.220(4) nm. The eKEs range from 0.5 – 50 meV with a photoelectron energy resolution in the 100’s $\mu$eV range. At the lowest eKE achievable where angular distributions can still be extracted, a photoelectron energy resolution of 266 $\mu$eV FWHM was achieved.

![Figure 2](image.png)

**Figure 2.** Photoelectron spectrum for photodetachment of $O^{-}$ ions with 832.220-nm linearly polarized light, together with the corresponding velocity-map photoelectron image (inset). The experimental spectrum (circles) has been fitted with Gaussian functions (lines). The FWHM resolution ranges from $\Delta E = 0.27 - 0.62$ meV as indicated above the first and last feature (left to right). The low intensity for the transitions originating from the $^{2}P_{1/2}$ anion state is a characteristic of the anion source.

Photodetaching a $p$ electron from $O^{-}$, as described by Eq. (1), results in the production of outgoing $s$ and $d$ partial waves. Rau and Fano [6] and Lineberger and Woodward [7] both treated this process theoretically for conditions near threshold, where $s$ waves dominate. They considered the final state as a $JJ$-coupled ($e$ + atom) complex created after the $LS$-coupled anion absorbs a photon. Rau [8] showed that under these conditions the fine-structure relative intensities are given by pure geometric factors, which do not involve the full photodetachment dynamics. A generalized theoretical treatment by Pan and Starace [9] for photodetachment showed that by using the approach of term-independent dynamical amplitudes often used in the central-potential model, factorization of the geometric and dynamical factors can be achieved, resulting in intensity ratios given by geometric factors.

The relative intensity ratios between the observed fine-structure transitions agree well with the theoretical values generated using the formalism of [9] and the previous measured values of [10, 11], except for the lowest eKE ($^{1}P_{0} \leftarrow ^{2}P_{3/2}$) transition in Fig. 2, which is suppressed. The suppressed intensity for the $^{3}P_{0} \leftarrow ^{2}P_{3/2}$ transition is the result of its proximity to threshold and can be accounted for by scaling the transition intensity according to the Wigner law for photodetachment, eKE$^{3/2}$ [12].
Once scaled according to the Wigner law the theoretical values are in excellent agreement with our experimental results.

Figure 3 shows the extracted branching ratio for transitions from the $^2P_{3/2}$ anion ground state to the $^1P_1$ and $^3P_2$ states of the neutral oxygen atom versus the eKE of the transition to $^3P_1$. The eKEs for this ratio range from 500 $\mu$eV – 1 eV. The branching ratio exhibits a trend typical of a cross-section for photodetachment, a sharp rise in the cross section from threshold levelling out to a value that is consistent with the intensity ratios given by the geometric factors. Fluctuation in the branching ratio above an eKE = 0.6 eV can be attributed to statistical variations and are not indicative of any physical behaviour. A tentative fit of the Wigner law, expressed as a ratio of each transition, i.e. $\sigma(^3P_1)/\sigma(^3P_2) \propto [eKE(^3P_1)/eKE(^3P_2)]^{1/2}$, has also been plotted for comparison and as a measure for the range of validity. The fit suggests the range of validity of the Wigner law extends from threshold to at least 13 meV. Further analysis of this and the other branching ratios will be published elsewhere.

Figure 3. The extracted branching ratio for transitions originating from the $^2P_{3/2}$ state of the anion to the $^1P_1$ and $^3P_2$ states of the neutral oxygen atom. Circles: this work. Solid line: Wigner Law for photodetachment of an $l=1$ orbital.

The angular anisotropy described by the $\beta$ parameter contains all the dynamics of the photodetachment process. This parameter was extracted from the photoelectron images by plotting electron intensity against $P_2(\cos \theta)$ and fitting to the well-known equation [13]:

$$\frac{d\sigma(E)}{d\Omega} = \frac{\sigma_{\text{total}}(E)}{4\pi} [1 + \beta(E) P_2(\cos \theta)],$$

where $E$ is the eKE, $\theta$ is the angle between the photon electric vector and the electron momentum vector, $\sigma_{\text{total}}$ is the total cross section for photodetachment, $\beta$ is the angular-distribution asymmetry parameter and $P_2(\cos \theta)$ is a Legendre polynomial of second order. Photodetachment of a $p$ orbital from atomic oxygen gives rise to $s$ and $d$ outgoing partial waves with the value of $\beta$ dependent on the intensity and relative phase shift between each partial wave.

Figure 4 shows the experimental $\beta$ values versus eKE for the $^3P_2 \leftarrow ^2P_{3/2}$ transition (circles) compared with the central-potential Cooper-Zare model [13] (solid curve) and a parameterised version of this model by Hanstorp et al. [14] (dashed and dotted curves). Also shown for comparison is the experimental data of Hanstorp et al., [14] (squares), Hall and Siegel [15] (diamond) and Breyer et al. [10] (triangles). It should be noted that the $\beta$ estimates for [14,15] are for unresolved fine-structure transitions and therefore are not strictly comparable to the current data set. They are shown as a guide to the relative accuracy of our $\beta$ values for eKEs higher than 0.24 eV. The experimental range of eKE in Fig. 4 is 480 $\mu$eV – 1.26 eV.
The parameterisation by Hanstorp et al. [14] provides an analytical expression for $\beta$ versus eKE with two adjustable parameters. With a simple assumption regarding the energy dependence of dipole radial matrix elements, $R_{\pm1}$, their parameterization yielded:

$$\beta(E) = \frac{2A_2^2E^2 - 4A_2Ec}{1 + 2A_2^2E^2},$$  \hspace{1cm} (3)$$

where $c = \cos(\delta_2 - \delta_0)$ is the relative phase shift between the $s$ and $d$ outgoing waves, $A_2E = R_2/R_0$ is the ratio of radial matrix elements and $E$ is the photoelectron eKE.

The two parameterised curves in Fig. 4 have the same value for the ratio between the radial matrix elements, set by fitting to the Cooper-Zare model [13], but different values for the relative phase shift between the two outgoing partial waves [1.0 (dotted curve), 0.925 (dashed curve)] [3]. The experimental values for $\beta$ with eKEs above 0.24 eV, lie closest to the dashed curve, the curve with the smaller phase-shift value, and then converge to a value common to all curves below this point until an eKE of 40 meV. The magnitudes of our data points are also consistent with the values of [14,15]. This suggests that, for eKEs higher than 0.24 eV, there may be slightly less phase shift between the two partial waves or a greater $s$-wave contribution than predicted by theory [13].

The convergence of data and theory for eKE between 40 meV and 0.24 eV clearly shows the decreasing $d$-wave contribution and is consistent with the Cooper-Zare formalism [13] which predicts that, as the eKE decreases, the outgoing electrons become more $s$-wave in nature and should tend to a completely isotropic distribution at zero eKE. However, below an eKE of 40 meV a slow and increasing turnaround towards lower values of $\beta$ is evident. Recent theoretical calculations by Kutzner et al. [16] and Roberston et al. [17] for photodetachment of atomic halogen anions, where correlation effects such as polarization and relaxation are taken into account, show a similar turnaround in the value of $\beta$ for outgoing electrons as eKE $\to 0$. Their conclusion is that, as the outgoing electron’s eKE becomes lower, electron correlation effects become more pronounced. Our results may show the effect of electron correlations at low eKE and, if so, would serve as a good test for the inclusion of electron correlation-effects into relativistic theoretical models for open-shell atoms.

4. Conclusions and future work
Preliminary results for the photodetachment of the atomic oxygen anion have been presented. They include the $^3P_1$ and $^3P_2$ branching ratio [i.e., $\sigma(^3P_1)/\sigma(^3P_2)$] for both transitions originating from the

![Figure 4. A comparison of the experimental and theoretical $\beta$ values for the $^3P_2 \leftarrow ^3P_{3/2}$ transition. Experimental data: (Circles) this work, (triangles) Breyer et al. [10], (squares) Hanstorp et al. [14] and (diamond) Hall and Siegel [15]. Theory curves: (Solid line) Cooper and Zare [13], (dotted and dashed lines) model of Hanstorp et al. [14] with phase shifts of 1.0 and 0.925, respectively.](image-url)
$^2P_{3/2}$ state of the anion and a measurement of the angular-distribution asymmetry parameter for eKEs across a wide range. The results were collected using a very high-resolution VMI spectrometer, which is coupled to an anion source and mass TOF spectrometer. The measurements of the $\beta$ parameter represent a new standard, not only due to the extensive range of the measurements, but more importantly, the lowest eKE for which a value of $\beta$ has been obtained. These measurements should prove to be a substantial test for theory and will hopefully act as an incentive for new and detailed calculations for the photodetachment of atomic oxygen, particularly relativistic calculations that include fine-structure detail, polarization and relaxation effects. The finalized data for O$^-$, including further results for the remaining fine-structure transitions, will be published elsewhere.

In the future, measurements on atomic sulfur will be undertaken across the same eKE range as undertaken on atomic oxygen. These measurements should not only add to the collective spectroscopic knowledge of a significant species but also provide a stronger test for relativistic theory, especially at threshold, given sulfur’s stronger dipole-polarizability.

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References
[1] Covington A M, Calabrese D, Williams W W and Thompson J S (1997) Phys. Rev. A 56 4746
[2] Andersen T (2004) Phys. Rep. 394 157
[3] Cavanagh S J, Gibson S T, Gale M N, Dedman C J, Roberts E H and Lewis B R (2007) Phys. Rev. A 76 052708
[4] Garand E, Buchachenko A A, Yacovitch T I, Szczesniak M M, Chalasinski G and Neumark D M (2009) J. Phys. Chem. A 113 4631
[5] Hansen E W and Law P -L (1985) J. Opt. Soc. Am. A 2 510
[6] Rau A R P and Fano U (1971) Phys. Rev. A 4 1751
[7] Lineberger W C and Woodward B W (1970) Phys. Rev. Lett. 25 424
[8] Rau A R P, Electron and Photon Interaction with Atoms, edited by Kleinpoppen H and McDowell M R C (Plenum, New York, 1976), Chap. 12
[9] Pan C and Starace A F (1993) Phys. Rev. A 47 295
[10] Breyer F, Frey P and Hotop H (1978) Z. Phys. A 286 133
[11] Suzuki T and Kasuya T (1987) Phys. Rev. A 36 2129
[12] Wigner E P (1943) Phys. Rev. 73 1002
[13] Cooper J and Zare R N (1968) J. Chem. Phys. 48 942
[14] Hanstorp D, Bengtsson C and Larson D J (1989) Phys. Rev. A 40 670
[15] Hall J H and Siegel M W (1968) J. Chem. Phys. 48 943
[16] Kutzner M, Robertson J A and Pelley P (2000) Phys. Rev. A 62 062717
[17] Robertson J A, Kutzner M and Pelley P (2001) Phys. Rev. A 63 042715