Control of Near-Threshold Detachment Cross Sections via Laser Polarization

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The behavior of near-threshold cross sections for dissociation of a target into a pair of particles, as described by Wigner's threshold law, can depend sensitively on the angular momentum of the particles. In this Letter, we investigate the near-threshold nonresonant two-photon detachment process in the negative ion of gold. The expected s-wave threshold behavior is observed with linearly polarized light. Closure of the s-wave channel is realized by using circular polarization, allowing the first observation of a d-wave threshold. Practical applications are discussed, including extensions which could prove valuable for investigations of negative ions with near-threshold structure.

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In 1948, Wigner developed general expressions describing the threshold behaviors of the cross section for dissociation of a target into a pair of particles [1]. If one or both particles produced are not charged, then usually [2] the interaction between the particles is shorter ranged than the centrifugal potential, $\ell(\ell + 1)/r^2$, and the cross section (σ) depends only on the relative linear (k) and angular (ℓ) momentum of the particles: $\sigma \propto k^{2\ell+1}$. This Wigner threshold law has been verified in countless experiments, and is commonly used in laser photodetachment threshold spectroscopy for high precision measurements of atomic negative ion binding energies (ε_0) [3]. In particular, for negative ion photodetachment $\sigma \propto \varepsilon^{\ell+1/2}$, where $\varepsilon = h\nu - \varepsilon_0 \propto k^2$ is the energy and ℓ is the angular momentum of the photoelectron.

If the excess electron of a negative ion is bound in an orbital with angular momentum ℓ_0, a single-photon detachment process ejects the photoelectron into at most two angular momentum channels: $\ell = |\ell_0 \pm 1|$. Furthermore, at sufficiently low photoelectron energies, the centrifugal barrier suppresses the higher angular momentum channel and the photoelectron exits in the lower partial wave. As might be expected, the Wigner law applies equally well if two or more photons are used to detach the negative ion. Both p-wave (in Cl^- [4] and Si^- [5]) and s-wave (in H^- [6]) thresholds have been observed experimentally in two-photon detachment. It is interesting to note that only s- and p-wave detachment thresholds have been observed in either single- or multiphoton detachment. For single-photon detachment, higher partial waves ($\ell \geq 2$) can dominate near the threshold only if the excess electron of the negative ion has $\ell_0 \geq 3$, e.g., detachment from an f or g orbital. There are therefore very few suitable species, and experimental considerations (small binding energies, low cross sections, poor ion currents, and radioactivity) make these ions unattractive. In contrast to single-photon detachment, the polarization of the light field can play an important role in multiphoton detachment. Indeed, measurements of the angular distributions of the ejected electron in multiphoton detachment can yield new features if observed with elliptically polarized light, and has become an area of recent interest [7]. In general, for an n-photon detachment process, partial waves with $\ell = |\ell_0 - n|, |\ell_0 - n + 2|, \ldots, |\ell_0 + n|$ are possible. If linearly polarized light is used, the lowest partial wave will again dominate near the threshold [8]. However, the use of circular polarization imposes $\ell = |\ell_0 \pm n|$, and can therefore give rise to a dramatic change in the photodetachment threshold behavior. A small polarization dependence in the Cl^- detachment cross section has been observed in a two-color experiment [9], but essentially only for two photon energies far above the two-photon threshold. The primary goal of the experiments presented in this Letter is to demonstrate the change in the threshold law with laser light polarization. We shall also discuss selected novel applications and extensions of this technique.

The tunable infrared laser light required for the experiment is produced by a 10 Hz Nd:YAG pumped dye laser, Raman shifted in a high pressure H_2 cell. In order to control the polarization, the laser light is directed through a rotatable, achromatic quarter-wave plate. The laser light then passes into a 15 cm focal length best-form lens and through a viewport into an ultrahigh vacuum chamber to focus onto an 8 keV, 500 nA beam of Au^-, extracted from a Cs sputter source. The laser and ion beams are orientated to intersect at 90°. Further details of the apparatus can be found elsewhere [5,10].

The high intensities and long wavelengths ($\lambda \approx 1$ μm) required for these experiments give rise to significant energy shifts, predominantly due to the ponderomotive shift [11]. The ponderomotive shift originates from the fact that a free electron undergoes an oscillatory motion in the high intensity light field [12]. As a result, the energy of the free electron state in a light field is increased by an amount equal to the ponderomotive potential $\Delta = e^2E^2/4m_e\omega^2 = I\lambda^2U_{\mathrm{pon}}$, where E, I, and $\omega = 2\pi\nu$ are, respectively, the electric field amplitude, intensity, and frequency of the light field, and

$U_{\text{pon}} = 7.53 \times 10^{-10}$ cm^{-1} μm^{-2} (W/cm^2)$^{-1}$. Initial experiments aimed at verifying U_{pon} yielded shifts much smaller than expected and resulted in a good deal of controversy on the subject (see [13] and references therein). These observations were explained in part by the phenomenon termed "leakage detachment" in very low frequency light fields [14], and by unfavorable experimental conditions [13,15]. Later, a careful experiment by Davidson *et al.* [13] demonstrated that the ponderomotive shift was consistent with the expected value.

It is important to further consider the effect of threshold shifts for our experimental conditions, as this improves the fit to the data. In a uniform light field, the threshold is shifted to higher energies by the ponderomotive potential and the Wigner law for n-photon detachment becomes $\sigma_n = a_n(nh\nu - \varepsilon_0 - \Delta)^{\ell+1/2}$, with a_n a constant [16]. In practice, the intensity of the light varies both in position and time, causing the threshold to smear out over a photon energy region $\approx\Delta/n$. The local n-photon detachment rate is: $dR_n = \sigma_n \Phi^n(x,y,z,t)\rho(x,y,z)dx\,dy\,dz$, with $\Phi = I/h\nu$ the photon flux and ρ the ion beam density. We assume that the laser pulse is propagating along the z axis, and has a Gaussian profile in the beam cross section (the x-y plane) with a full width at half maximum (FWHM) Γ_x and Γ_y, and a Lorentzian profile in time (t) with a FWHM Γ_t. Since the laser beam is approximately cylindrical in symmetry over the interaction volume with a focus waist much smaller than the width of the ion beam, ρ can be taken as constant in the x-y plane, and integration over z only introduces an overall constant. Finally, the pulse-to-pulse variations in pulse energy were found to obey the statistics of a normal distribution, and is therefore modeled with a Gaussian having a FWHM $\Gamma_\xi = 16\%$ of the mean pulse energy. Transforming to the (reduced) cylindrical coordinate system, $\tilde{r}\cos\theta = x/\Gamma_x$, $\tilde{r}\sin\theta = y/\Gamma_y$, and $\tilde{t} = t/\Gamma_t$, and integrating over z and θ, the signal $S_n \propto \int R_n\,dt$ is given by

$$\frac{S_n(h\nu)}{I_p^n} = a\int_{-\infty}^{+\infty}\int_0^{\infty}\int_0^{\infty} \tilde{r}\tilde{I}^n\sigma_n(h\nu;b)\,d\tilde{r}\,d\tilde{t}\,\varrho\,d\xi\,. \qquad (1)$$

Here, $\varrho(\xi) = \varrho_0\exp(-4\ln 2\xi^2/\Gamma_\xi^2)$ is the probability density of having a pulse with peak intensity $(1+\xi)I_p$, $\tilde{I}(\xi,\tilde{t},\tilde{r}) \equiv I/I_p = (1+\xi)(4\tilde{t}^2+1)^{-1} \times \exp(-4\ln 2\tilde{r}^2)$ is the intensity profile of the pulse, and $\sigma_n(h\nu;b)$ is the cross section for n-photon detachment which may be given by the Wigner law or some more general expression (see below). Finally, the amplitude a and the ponderomotive parameter $b = I_pU_{\text{pon}}$ are fitting parameters (note that $\Delta = \tilde{I}\lambda^2 b$). The shape of the threshold is then independent of the spatial and temporal scale of the experiment. However, these geometrical parameters are necessary to extract U_{pon} from the fitted value of b. This can be done by deducing I_p from the measured pulse energy:

$$E_{\text{pul}} = \iiint I\,dx\,dy\,dt = \left(\frac{\pi^2}{8\ln 2}\right)\Gamma_x\Gamma_y\Gamma_t I_p\,. \qquad (2)$$

Using parameters typical for the geometry of the present experiments, $E_{\text{pul}} \approx 8$ mJ, $\Gamma_x = \Gamma_y \approx 25$ μm, and $\Gamma_t \approx 8$ ns, we obtain $I_p \approx 9 \times 10^{10}$ W/cm^2.

In practice, the pulse energies vary as the laser is tuned in wavelength. Therefore, I_p depends weakly on $h\nu$. In addition, there is a small $(n+1)$-photon excess photon detachment (EPD) background, which depends on I_p^{n+1}. Noting that $I_p(h\nu) \propto E_{\text{pul}}(h\nu)$ by Eq. (2) and specializing to $n = 2$, we correct the data for pulse energy variations and EPD using $S_c(h\nu) = [S(h\nu) - A_3E_{\text{pul}}^3(h\nu)]/E_{\text{pul}}^2(h\nu)$, where $S(h\nu)$ is the observed signal and A_3 is a constant such that $A_3E_{\text{pul}}^3(h\nu)$ is the estimated three-photon detachment signal, assuming the cross section remains constant and equal to the below-threshold value ($\approx$3% of the signal obtained at 9380 cm^{-1}). We found that the below-threshold signal (at 9212 cm^{-1}) depended on pulse energy according to $E_{\text{pul}}^{2.9(3)}$, consistent with three-photon detachment (all uncertainties are quoted to one standard deviation, unless otherwise noted). We then have that $S_c(h\nu) \propto S_2/I_p^2$, given by Eq. (1). The variations of I_p with wavelength also introduce a more subtle error in the measurements. As the laser pulse energy changes, so does the ponderomotive shift, which produces an effective uncertainty in the energy position of the data points. The horizontal error bars in the figures reflect the full relative shift expected from these variations.

Figure 1 presents the data from measurements of the threshold region using linearly polarized light. The fit of Eq. (1) to the data yields $b = 49(3)$ cm^{-1} μm^{-2},

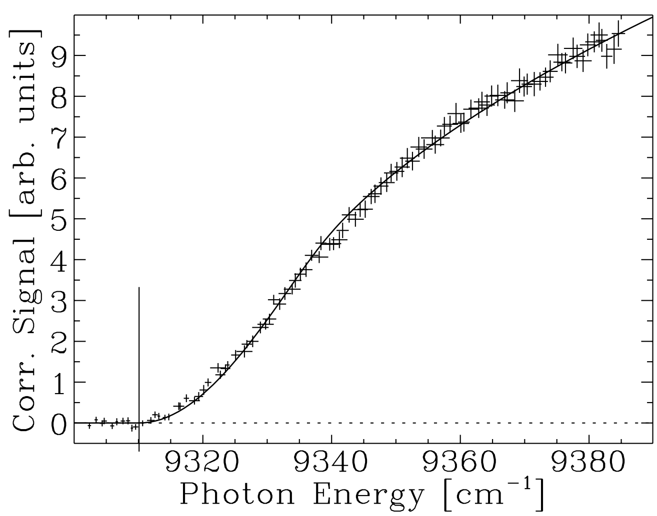

FIG. 1. Detachment signal near the two-photon threshold in Au$^-$. The data are corrected for variations in pulse energies ($\approx$5% over this region) and three-photon EPD background. Vertical error bars represent 80% confidence limits based on observed statistical scatter; horizontal error bars are discussed in the text. The fitted curve is based on a shifted Wigner threshold law for s-wave detachment. A vertical line indicates the position of the nominal two-photon threshold ($h\nu = \varepsilon_0/2$).

assuming the known binding energy of Au$^-$, $\varepsilon_0 = 18\,620.2(2)$ cm^{-1} [3,17]. The small systematic deviations of the model from the data are likely due to additional smearing of the threshold from some details not included in the model, such as the hyperbolic shape of the focus waist, the ion density distribution, a possibly imperfect (i.e., non-Gaussian) laser focus profile, and a more complicated temporal profile. The otherwise excellent general agreement of the model with the data indicates that this technique could be used to obtain high precision measurements of the ponderomotive shift, assuming good characterization of the laser pulse parameters.

We now consider the polarization dependence of the two-photon detachment cross section. Figure 2 presents the data obtained with linearly and circularly polarized light. The remarkable difference in the curves can be entirely explained by the change in the centrifugal potential encountered by the ejected electron. As discussed earlier, for two-photon detachment with linearly polarized light, the photoelectron is ejected with angular momentum $\ell = \ell_0$ or $|\ell_0 \pm 2|$. In the case of Au$^-$, $\ell_0 = 0$ and therefore $\ell = 0$ or 2. Near the threshold, the centrifugal potential for d-wave detachment effectively suppresses that channel, and a Wigner s-wave law is observed. The solid curve is obtained from Eq. (1) using $\sigma_2 = a_2(2h\nu - \varepsilon_0 - \tilde{I}\lambda^2 b)^{1/2}$, with the amplitude as the only free parameter. The curve fits the data near the threshold well, but begins to diverge at higher photon energies and was observed to lie ≈30% above the data at photon energies ≈6% above threshold. The breakdown of the Wigner law is expected, and has been studied in a number of single-photon detachment experiments [17,18] and theoretical treatments [19]. To our knowledge, there has been no experimental work aimed at studying the range of validity of the Wigner law in multiphoton detachment. Recently, Gribakin and Kuchiev [20,21] have obtained general expressions for multiphoton detachment cross sections. The dotted curve in Fig. 2 shows the two-photon detachment signal using Eq. (1) with σ_2 given by their theory, modified to include the effect of threshold smearing. Although the theory appears to predict a somewhat premature breakdown of the Wigner threshold law, the expected accuracy of the theory for two-photon detachment is consistent with the observed deviation [21].

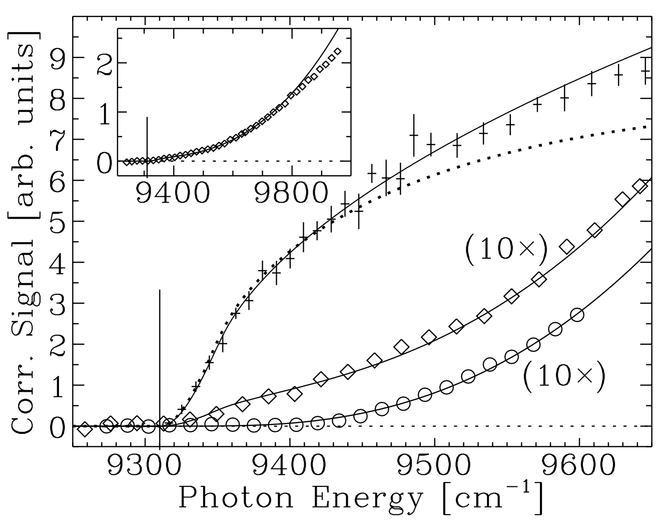

FIG. 2. Corrected signal obtained using linearly (+), elliptically (◇), and circularly (○) polarized light. The scale for the ◇ and ○ data sets has been magnified by a factor of 10. We estimate a 30% uncertainty in the scale of the linear relative to the circular and elliptical data sets. The height of the + symbols indicate 80% confidence limits; errors for the ◇ and ○ data are smaller than their height. Errors in photon energy are smaller than the width of the symbols. The full curves are based on the Wigner law, while the dotted curve is based on theory by Gribakin and Kuchiev, scaled to agree with the near-threshold data. The nominal two-photon threshold is marked by a vertical line. A scan of the ◇ data covering a larger range is shown in the inset.

Using circularly polarized light, photons with only one spin orientation are available and the photoelectron can be ejected into the $\ell = |\ell_0 \pm 2| = 2$ partial wave only, i.e., as a d wave. The data denoted with open circles (○) in Fig. 2 were obtained using a quarter-wave plate adjusted for circularly polarized light. The excellent fit to the Wigner d-wave law [Eq. (1) with $\sigma_2 = a_2'(2h\nu - \varepsilon_0 - \tilde{I}\lambda^2 b)^{5/2}$] indicates that little or no s-wave component is present over a large energy region. We estimate that the s-wave detachment cross section has been suppressed to ≲0.5% of that observed for linear polarization. To verify this signal was indeed from a two-photon process, we measured the dependence of the signal on pulse energy at 9635.4 cm^{-1}, and found that $S \propto E_{\mathrm{pul}}^{2.3(2)}$; an exponent slightly larger than 2 may be due to the small EPD background.

Figure 2 also shows data (diamonds) obtained with a small adjustment of the quarter-wave plate (≈1°), corresponding to slightly elliptically polarized light. The near-threshold data are systematically above the d-wave curve due to the introduction of a small amount of s-wave detachment. To obtain the solid curve following these data, we added 2% of the linear polarization signal to the d-wave model. As can be seen in the inset, this model is in good agreement up to photon energies ≈9750 cm^{-1}, i.e., ≈5% above the threshold. The eventual departure from the Wigner law far above threshold is expected and is also seen in single-photon s- and p-wave detachment [17–19], as noted above.

In conclusion, we have shown that it is possible to dramatically change the energy dependence of the near-threshold cross section in two-photon detachment. These measurements have led to the first observation of a Wigner d-wave law in a negative ion. Higher partial waves could be studied with higher order processes; for example, a three-photon process could be made to yield an f wave.

The technique demonstrated here can be directly applied or naturally extended to study a range of interesting structures in negative ions. Two-photon detachment offers a convenient control over the magnitude of the threshold signal and, in some cases, a way to effectively "switch on" (or off) a structure lying near the threshold. The two-photon threshold signal could be greatly reduced (by using circularly polarized light) in order to better observe a near-threshold structure. For example, the $4d^9 5s^2\ {}^2D_{3/2}$ excited state of Pd^- is expected to be bound by $50 \pm 350\ \mathrm{cm}^{-1}$ [22] placing it in the vicinity of the $4d^{10}5s\ {}^2S_{1/2} \rightarrow 4d^{10}\ {}^1S_0$ ground state detachment threshold. An attempt to detect this excited state in a single-photon magnetic dipole resonance experiment was unsuccessful [10], and may be an indication that it is slightly unbound. While the state should be visible as a two-photon electric dipole ($E1$) resonance, it is unlikely that such a feature would be observable on top of the two-photon s-wave detachment signal. The use of circularly polarized light would greatly reduce the near-threshold signal while simultaneously increasing the signal from the resonance, thus significantly improving the detection sensitivity. Another important example is provided by Os^-, where an unwanted structure could be eliminated with two-photon detachment. A very strong $E1$ resonance lying only 3.5 meV above the ground state detachment threshold results in a situation that is unfavorable for an accurate determination of the electron affinity of Os [23]. Since this resonant transition would be strongly forbidden under two-photon detachment, a "clean" s-wave threshold could be observed. An accurate determination of the threshold value would then be possible, assuming a good characterization of threshold shifts. W^- [23], Cs^- [24], and He^- [25] have a similar near-threshold $E1$ structure, and may also benefit from such an approach.

As a final note, in some experiments accurate knowledge of the magnitude of the threshold shift [11] may be required. Previous investigations of the ponderomotive shift in negative ions have been conducted in the presence of two laser fields: a high intensity, low frequency field (infrared or microwave) to produce the shift, and a high frequency field to detach the ions. Because good overlap of the light fields is crucial, the use of two fields can complicate experiments, and likely gave rise to some of the discrepancies observed in early studies [13]. As we have demonstrated here, using a single light field makes the process easier to model and eliminates these focus matching problems, thus offering a simple and effective method to accurately measure the magnitude of the shift which could be exploited in future work.

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