# Photoelectron imaging: an experimental window into electronic structure

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Photoelectron imaging is finding increasingly widespread use in probing electronic structure and chemical dynamics. In this *tutorial review*, two benchmark systems,  $H^-$  and  $I^-$ , are used to introduce essential concepts linking photoelectron images of negative ions with parent electronic structure. For pedagogical reasons, a qualitative approach based upon spectroscopic selection rules is emphasized in interpreting the images. This approach is extended to molecular systems, highlighting that even qualitative interpretation of results can lead to significant chemical insights.

# 1. Introduction

Recent advances in charged particle imaging have revolutionized the field of gas-phase reaction dynamics.<sup>1,2</sup> These powerful techniques employ a "photographic" approach to reveal the properties of photoelectrons or photofragments ejected from molecular species. Photoelectron imaging, in particular, provides insight into the bonding structures that hold molecules together.

Charged particle imaging was first applied to gas-phase neutral-molecule photodissociation.<sup>1</sup> Photoionization of the fragments followed by electrostatic projection onto a position-sensitive detector yielded a two-dimensional snapshot of the three-dimensional nascent momentum distribution.<sup>3</sup> The translational energy spectrum and angular distribution of the nascent photoproducts could thus be determined simultaneously.

This general approach has since been applied to measure energy partitioning, as well as scalar and vector correlations in various experimental contexts, including photodissociation, photoionization and photodetachment, reactive and inelastic collisions.<sup>4–8</sup> In particular, the time-resolution allowed by an ultrafast pump–probe scheme is a powerful enhancement of the technique allowing tracking of electronic structural evolution for reacting molecules on the natural timescale of atomic motions.<sup>9–11</sup>

In this paper, we provide a tutorial overview of photoelectron imaging aimed at upper level students, science educators, and researchers previously unfamiliar with this technique, by drawing on results of our anion photodetachment experiments. In the interest of brevity and clarity, we limit discussion to the core ideas underlying photoelectron imaging and refer readers primed with the fundamentals of the technique and interested in time-resolved applications to references such as ref. 11 and 12.

A typical photoelectron imaging detection arrangement is illustrated in Fig. 1. The photoelectron image shown was obtained in 800 nm photodetachment of  $CS_2^-$  (discussed in Section 5). Typically, each experimental cycle, consisting of the interaction of a mass-selected packet of anions with a linearly polarized, collimated, pulsed laser beam, results in several photodetachment events within the small laser–ion interaction volume. For the purpose of this discussion, the



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Fig. 1 Schematic illustration of the photoelectron imaging arrangement. (a) Electrons are detached from anions at the intersection of the ion and laser beams and projected onto the detector by an electric field applied *via* the imaging electrodes. The photoelectron cloud can be visualized as a continuous progression of nested expanding spheres (b). The experimental image (c) was obtained using 800 nm photons detaching electrons from  $CS_2^-$ . In general, images represent 2-D projections of the electron distributions. The laser polarization (which defines the cylindrical symmetry axis, *z*) lies parallel to the plane of the detector.

interaction volume can be presumed to be nearly point-like. The nascent photoelectron speed v is determined by the light frequency v and the electron binding energy eBE, according to

$$mv^2/2 = h\nu - eBE \tag{1}$$

The electron displays dual wave-particle characteristics. Viewed as particles, the emitted electrons scatter in various

directions from their origin. Viewed as waves, within tens of nanoseconds following photodetachment, the free-electron wavefront expands from the molecular scale (ångströms) to macroscopic dimensions at a speed defined by eqn (1). Simultaneously, the electrons are projected toward the detector using an arrangement of external electric fields. The photoelectron image accumulated over many laser pulses maps the density of electron impacts on the detector and represents a 2-D projection of the 3-D photoelectron velocity distribution.

In general, the experimental observables are related to the electronic structure in terms of the time-independent Schrödinger equation. The photoelectron spectrum reflects energy eigenvalues of the parent atomic or molecular system, while the photoelectron angular distributions reveal characteristics of the corresponding wavefunctions. Recent years have seen parallel advances in theoretical modeling  $^{\rm 13-15}$  and the emergence of simple conceptual models explaining the nature of the experimental findings.<sup>8</sup> These latter models consider the interference between emitted electron waves at a level sufficient to illuminate the physical essence of the observed phenomena, without invoking more complete yet often daunting mathematical treatments. In this article we will use the benchmark cases of H<sup>-</sup> and I<sup>-</sup> to introduce the fundamentals of photoelectron imaging and outline the concepts behind the qualitative models which have proved invaluable in the interpretation of results. We will also discuss the extension of these general concepts to molecular anions.

## 2. Acquisition of photoelectron images

A typical negative-ion photoelectron imaging experiment involves three stages: ion formation, mass-selection, and photodetachment probing of the selected species. Experiments are typically performed in pulsed mode. In our case, each experimental cycle involves a short (<100 ns) pulse of anions overlapping with a much shorter photon pulse ( $\sim100$  fs or several ns). Generally, a number of detachment events occur within the laser–ion interaction volume per experimental cycle. Here we concentrate on details of the imaging arrangement,



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In the idealized case of a monoenergetic electron and in the absence of an external field, the position of the photoelectron at a given time t (measured from the photodetachment event) will lie on the surface of a sphere of radius vt. The center of the sphere coincides with the photoelectron origin. From the quantum mechanical perspective, the probability distribution of the position of the electron on the surface of the sphere conforms to  $|\psi|^2$ , where  $\psi$  is the photoelectron wavefunction. Only when the position is *measured*, can we talk about a localized position of the electron. Suppose for a moment that we employ a spherical position-sensitive detector surrounding the photoelectron origin. Measurement with this detector will locate the electron at a particular point on the sphere. That is, the act of measurement collapses the delocalized probability distribution on the single point of observed electron impact. Repetitions of the experiment under exactly the same conditions generally yield different impact positions. A large number of such repetitions will eventually map out the  $|\psi|^2$ probability density on the surface of the detector.

In reality a spherical detector is impractical for photoelectron spectroscopic measurements. Instead, the inherent charge of the electron allows the use of electric fields to collect all of the photoelectrons by accelerating them towards a planar detector located some distance away from the photodetachment origin (see Fig. 1). The detector usually consists of a pair of microchannel plates acting as a position-sensitive electron multiplier, equipped with a phosphor screen. Impacts appearing on the screen are accumulated using a digital camera.

For a point electron source and uniform electric field directed along the y axis, which is perpendicular to the detector plane (xz), this accumulation would eventually yield a 2-D projection of the 3-D probability density onto the detector. Furthermore, since the applied field is perpendicular to the detector face the image would also represent the velocity distribution within the xz plane. For multiple electron sources (ions spread throughout the interaction volume), any image recorded using a uniform field directed along y will consist of a series of overlapping velocity distributions, resulting in spatial blurring. The "velocity mapping" electrode arrangement first introduced by Eppink and Parker<sup>2</sup> minimizes this problem. The three electrodes shown in Fig. 1 create an inhomogeneous electric field. In classical terms we might think of this as funneling electrons onto specific points on the detector, which depend only on the velocity vector, regardless of the starting point. In quantum mechanical terms the part of the probability density corresponding to a particular electron velocity is mapped onto a specific point on the detector (the reader is referred to ref. 2 for a full description). Within this "velocity mapping" arrangement the final image represents the momentum-space distribution of the electrons in the plane of the detector. $^{2,17}$ 

The photoelectron distribution produced with a polarized (or even an unpolarized, but directional) laser beam is not necessarily isotropic. It is these anisotropic characteristics of photodetachment that enable one to gain insights into the symmetry properties of the parent-ion electron orbitals and the dynamics of the detachment process. For linear polarization, the electric field vector  $(\varepsilon_p)$  defines a unique axis in space (z). The resulting 3-D velocity distribution of the photoelectrons varies with respect to  $\theta$ , the angle between the electron velocity vector and the z axis, but is cylindrically symmetric about z. The cylindrical symmetry allows a mathematical reconstruction of the nascent 3-D velocity distribution from its 2-D projection onto the detector plane using the inverse Abel transformation.

# 3. The photoelectron image

The following discussion is based on the photoelectron images shown in Fig. 2 and 3, corresponding to the photodetachment of  $H^-$  at 800 nm and  $I^-$  at 267 nm, respectively. For  $H^-$ , a similar 796 nm result was reported by Reichle *et al.*<sup>18</sup>

The process of image acquisition makes a compelling illustration of the Born interpretation of the wavefunction and also demonstrates the nature of measurement in quantum mechanics. As discussed in the previous section, individual electrons are observed as localized impacts on the detector surface (Fig. 2a). With limited statistics, the impact spots appear randomly distributed, but after many experimental cycles, a pattern emerges (Fig. 2b) reflecting the probability density distribution. The radial intensity distributions in these



**Fig. 2** Photoelectron imaging of H<sup>-</sup> at 800 nm. (a) An image accumulated for 7 laser pulses, showing ~10 randomly distributed electron impacts (seen as bright spots). (b) 140 experimental cycles. (c)  $1.1 \times 10^5$  experimental cycles. The image is a 2-D projection of the 3-D distribution, which can be recovered from the inverse Abel transformation, shown in (d). The photoelectron spectrum (e) and the angular distribution (f) are extracted from the inverse Abel transformed image. The laser polarization is vertical in the figure plane.



**Fig. 3** Photoelectron imaging of I<sup>-</sup> at 267 nm. (a) The photoelectron image. (b) Inverse Abel transformation. The two distinct rings correspond to the different peaks in the photoelectron spectrum (c). The photoelectron angular distribution (d) corresponding to the  ${}^{2}P_{3/2}$  transition peaks at  $\pi/2$ , in contrast to the H<sup>-</sup> detachment in Fig. 2 and contrary to classical expectations.

images show sharp maxima, while the angular distributions are distinctly anisotropic with respect to the laser polarization direction. We will use these results to illustrate the basics of image analysis and interpretation.

#### 3.1 The photoelectron spectrum

In the Abel-inverted image, the electron speed is proportional to the distance r from the center. Integration over  $\theta$  at each particular r yields the radial distribution, or the photoelectron momentum spectrum, which can be converted to the conventional photoelectron energy spectrum via Jacobian transformation. The spectra of H<sup>-</sup> and I<sup>-</sup> in Fig. 2e and 3c are shown as functions of electron kinetic energy (eKE).

The peaks in a photoelectron spectrum correspond to electron ejection accompanied by the population of specific energy levels of the residual neutral. The single peak in the photoelectron spectrum of  $H^-$  is due to the removal of an electron from the fully populated 1s orbital yielding the  ${}^2S_{1/2}$  ground state of the neutral atom.

For I<sup>-</sup>, two spin–orbit states, significantly different in energy, are accessed upon removal of a p-electron using 267 nm radiation. The higher-eKE peak corresponds to photoelectrons produced in coincidence with the ground ( ${}^{2}P_{3/2}$ ) electronic state of the iodine atom, while the lower peak corresponds to the excited state ( ${}^{2}P_{1/2}$ ). The 0.94 eV spacing between the peaks reflects the magnitude of the spin–orbit interaction in the iodine atom. The relative integrated peak intensities are proportional to the transition probabilities, including the degeneracies of the  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$  states of iodine.<sup>19</sup> The finite peak widths in the energy domain reflect experimental broadening factors, such as laser linewidth, parent-ion velocity spread, *etc.*<sup>16</sup>

#### 3.2 The photoelectron angular distribution

The photoelectron angular distribution (PAD) is obtained by integrating the intensity of the Abel-inverted image over a chosen spectral (*i.e.* radial) range. By inspection, the H<sup>-</sup> PAD (Fig. 2f) has a "parallel" character, peaking at  $\theta = 0$  and  $\pi$ , while the I<sup>-</sup> PADs (Fig. 3d) for both detachment channels peak at  $\theta = \pi/2$ , corresponding to "perpendicular" photodetachment transitions.

The PADs in one-photon photodetachment with linearly polarized light are generally described by the function:<sup>20</sup>

$$I(\theta) = (\sigma/4\pi) \left[1 + \beta P_2(\cos\theta)\right], \qquad (2)$$

where the proportionality constant  $\sigma$  corresponds to the total photodetachment cross-section and  $P_2(\cos\theta) \equiv 1/2(3\cos^2\theta - 1)$ is the second-order Legendre polynomial. The angular dependence is completely defined by  $\beta$ , the anisotropy parameter, which can be determined by fitting eqn (2) to the experimental PAD. The  $\beta$  values range from -1 to +2, with negative and positive values corresponding to perpendicular and parallel polarization, respectively. The  $\beta$  value observed in H<sup>-</sup> photodetachment is very close to the +2 limit of a purely parallel transition. For I<sup>-</sup> photodetachment, however, the rings in Fig. 3(a) correspond to  $\beta \approx -0.6$ .

#### 4. Interpreting photoelectron images

# 4.1 Relating photoelectron angular distributions to parent orbitals: the $H^-$ example

In a pulsed laser experiment the electron is described by a superposition of waves spanning a finite energy range. In the laboratory frame, this wavepacket is described as:

$$\Psi(r,\theta,\phi,t) = \int a(k)\Psi_k(r,\theta,\phi,t)dk$$
(3)

where a(k) is a shape function related to the laser lineshape. Assuming a central, *i.e.* spherically symmetric, potential  $\Psi_k(r,\theta,\phi,t)$  can be separated into radial and angular components,

$$\Psi_k(r,\theta,\phi,t) = R_k(r,t)Y(\theta,\phi) \tag{4}$$

The time dependence is carried in the radial function and the corresponding electron probability density can be likened to a pattern on a spherical balloon. As the "balloon" is inflated, the pattern expands, but its angular dependence remains unchanged.

The connection between a photoelectron image and the parent orbital can be demonstrated using three different (yet closely inter-related) approaches based on: (1) angular momentum conservation; (2) transition dipole moment operations; (3) general symmetry considerations. In the following, we adopt the one-electron picture of photo-detachment and discuss the uniquely simple case of  $H^-$  to illustrate the key ideas in photoelectron image interpretation.

**4.1.1 Conservation of angular momentum.** The selection rule for one-photon, one-electron atomic transitions is  $\Delta \ell = \pm 1$ , where  $\ell$  is the orbital angular momentum quantum number. In detachment from the hydrogen 1s orbital ( $\ell_i = 0$ ), the free-electron wave is characterized by a single  $\ell$  value of 1, corresponding to a p wave.

The magnetic quantum number, *m*, describes the projection of the orbital angular momentum of the electron on the quantization (z) axis. The use of linearly polarized light imposes the constraint that *m* must remain unchanged. Hence, in photodetachment from the 1s orbital, only the m = 0component of the  $\ell = 1$  free-electron wave is allowed. The  $\ell = 1$  and m = 0 quantum numbers correspond to a  $p_z$  wave, whose normalized angular dependence is described by  $Y_{1,0}(\theta,\phi) = (3/4\pi)^{1/2}\cos\theta$  (a single spherical harmonic) yielding a  $\propto \cos^2\theta$  probability distribution. This distribution corresponds to eqn (2) with  $\beta = 2$ , and agrees well with the  $\beta = 1.92 \pm 0.04$  value determined experimentally (Fig. 2).

**4.1.2 Transition dipole moment.** A transition is allowed under the electric-dipole approximation if the transition dipole moment, M, does not vanish:

$$\boldsymbol{M} = \langle \boldsymbol{\psi}_{\mathrm{f}} | \hat{\boldsymbol{\mu}} | \boldsymbol{\psi}_{\mathrm{i}} \rangle \neq 0 \tag{5}$$

Here,  $\hat{\mu} = -e\hat{r}$  is the dipole operator, while  $\psi_i$  and  $\psi_f$  designate the initial and final states of the electron at the time of the transition (t = 0). Since the transition amplitude is proportional to the scalar product of M and the laser electric field vector, for z-polarized light, one need only be concerned with the z component of the transition dipole moment:

$$\boldsymbol{M}_{z} = -e\langle \boldsymbol{\psi}_{\mathbf{f}} | z | \boldsymbol{\psi}_{\mathbf{i}} \rangle \neq 0 \tag{6}$$

For H<sup>-</sup>, the normalized angular component of  $\psi_i$  (1s orbital) is described by  $Y_{0,0}(\theta,\phi) = (1/4\pi)^{1/2}$ . The free-electron wavepacket can be expanded in any complete basis set, with the angular dependence most naturally described in terms of the spherical harmonics  $Y_{\ell,m}(\theta,\phi)$ , just as for bound atomic orbitals, as we have done in Section 4.1.1. From eqn (6), the harmonics contributing to H<sup>-</sup> photodetachment must satisfy  $\langle Y_{\ell,m}(\theta,\phi)|z|Y_{0,0}(\theta,\phi)\rangle \neq 0$ , restricting the photoelectrons to  $\ell = 1$  and m = 0, *i.e.* the  $p_z$  wave. This argument is illustrated pictorially in Fig. 4. The  $p_x \leftarrow s$  and  $p_y \leftarrow s$ transitions, producing x and y polarized p waves, are forbidden since  $\langle p_x|z|s \rangle = \langle p_y|z|s \rangle = 0$ .

**4.1.3 General symmetry properties.** In terms of symmetry, the non-zero requirement for M can be satisfied only if the direct product of the irreducible representations corresponding to  $\psi_f$ ,  $\hat{\mu}$  and  $\psi_i$  contains the totally symmetric representation for the symmetry point group to which the molecular or atomic system in question belongs. The spherical symmetry of H<sup>-</sup> corresponds to the full-rotation ( $K_h$ ) point group. The bound 1s orbital and the emitted p-electron waves transform according to the  $S_g$  (totally symmetric) and  $P_u$  irreducible representations, respectively, while the *z* component of the dipole moment operator also transforms as  $P_u$ . Therefore, for an allowed detachment with *z*-polarized light, the free-electron



Fig. 4 Pictorial representation of the transition dipole moment integral for detachment from the 1s orbital.

wavefunction must belong to the same irreducible representation as the direct product  $\Gamma(\psi_i) \otimes \Gamma(\mu_z) = S_g \otimes P_u$ , which gives  $P_u$ . The free-electron wavefunction emitted in the photodetachment of H<sup>-</sup> must transform under the  $P_u$  representation. Of all waves with defined  $\ell$  values, this corresponds exclusively to p functions, of which only  $p_z$  satisfies both the inequality in eqn (6) *and* the angular momentum considerations discussed earlier.

#### 4.2 Partial wave interference

Classical theory predicts that the electric field of the light should eject the photoelectrons predominantly parallel to the field direction, *i.e.* along the laser polarization axis. While this is in agreement with the results of  $H^-$  detachment, many experimental observations contradict this prediction,<sup>7,21–23</sup> the benchmark case of  $I^-$  being one example. The discrepancy highlights the importance of a quantum interpretation of photodetachment.

In general the photodetached electron will have two possible  $\ell$  values:  $\ell = \ell_i + 1$  and  $\ell_i - 1$ , where  $\ell_i$  is the angular momentum of the initial (bound) atomic orbital. In the case of I<sup>-</sup>, the emitted electron originates from a 5p orbital ( $\ell_i = 1$ ) and is therefore described as a superposition of s and d partial waves. The interference between these waves is key to understanding the detachment process, even though it renders some of the arguments made for the H<sup>-</sup> case difficult to visualize.

The quantitative aspects of angular distributions arising from interference of partial waves were considered by Bethe.<sup>24</sup> His expression for  $\beta$  variation with eKE for a one-electron atom was later generalized to many-electron atoms by Cooper and Zare.<sup>25</sup> The generalized Bethe equation, most commonly referred to as the Cooper–Zare formula in the modern chemical physics context, is used for modeling photoelectron angular distributions.<sup>26,27</sup> Unfortunately, it is too abstract for intuitive interpretation. Here, we focus on the qualitative aspects of I<sup>-</sup> photodetachment using a more visual approach to connect the properties of the parent atomic orbitals and resulting partial wave interference.

The initial wavefunction for the 5p electron is a superposition of the  $\ell_i = 1$ ,  $m_i = 0$ ,  $\pm 1$  states. Invoking the selection rules  $\Delta \ell = \pm 1$  and  $\Delta m = 0$  gives rise to three detachment channels, based on the *m* value, as described by the following:

$$\psi_{m=-1}(r,\theta,\phi,t) = C_{2,-1}R_2(r,t)Y_{2,-1}(\theta,\phi)$$
  

$$\psi_{m=0}(r,\theta,\phi,t) = C_{0,0}R_0(r,t)Y_{0,0}(\theta,\phi) + C_{2,0}R_2(r,t)Y_{2,0}(\theta,\phi)$$
  

$$\psi_{m=+1}(r,\theta,\phi,t) = C_{2,+1}R_2(r,t)Y_{2,+1}(\theta,\phi)$$
(7)

The coefficients  $C_{\ell,m}$  are related to the corresponding transition moments producing a particular partial wave. The qualitative features of the overall PAD can be considered by treating the probability density of the free electrons as a combination of individual m = -1, 0, 1 channels. Assuming equal populations of the  $\ell_i = 1$ ,  $m_i$  states,

$$I(\theta) \propto |\psi_{m=-1}|^2 + |\psi_{m=0}|^2 + |\psi_{m=1}|^2$$
(8)

A similar combination of *all* possible d waves with equal amplitudes would yield a spherically symmetric photoelectron distribution, as  $\Sigma_{m=-\ell}^{\ell} |Y_{\ell,m}(\theta,\phi)|^2 = (2\ell + 1)/4\pi$  for any

given  $\ell$ , as would the s wave considered on its own. Since m is limited to  $0, \pm 1$ , one might expect the angular distribution in the I<sup>-</sup> case to be determined by the "missing"  $\ell = 2, m = \pm 2$ partial waves. This argument is similar to describing a nearly filled atomic sub-shell (e.g.,  $p^5$ ) in terms of a single hole ( $p^1$ ). However, the "missing"  $Y_{2,\pm 2}(\theta,\phi)$  spherical harmonics would correspond to a reduction in intensity towards  $\theta = \pi/2$ , contrary to experiment. This difficulty highlights the importance of accounting for interference between allowed partial waves for even a qualitative agreement with the observations. As an added complication, both the radial and angular contributions must be taken into account. To further simplify this discussion, we set  $R_0^2 = R_2^2 = R^2$  in eqn (7). The  $C_{\ell,m}$  coefficients in (7) are uniquely determined by the corresponding quantum numbers<sup>25</sup> and for brevity we absorb these constants into the corresponding angular functions, renormalizing each spherical harmonic. Eqn (8) can then be expanded to explicitly show the effect of the angular and radial parts of the corresponding waves,

$$I(\theta) = R^{2}[|Y_{0,0}|^{2} + |Y_{2,-1}|^{2} + |Y_{2,0}|^{2} + |Y_{2,1}|^{2} \pm 2(Y_{0,0}*Y_{2,0})]$$
(9)

The sign in front of the cross term  $(Y_{0,0}*Y_{2,0})$  depends on whether the positive or negative roots of  $R_0^2$  and  $R_2^2$  are appropriate.

Fig. 5(a) illustrates the  $Y_{\ell,n} \times Y_{\ell',n'}$  terms in eqn (9). Graduate chemists should recognize the probability densities associated with the angular parts of s and d orbital functions. It is relatively straightforward to visualize how combining



Fig. 5 Visualizing I<sup>-</sup> photodetachment. I<sup>-</sup> photoelectron images represent a combination of the probability densities of the free electron emitted from initial states with  $\ell = 1, m = 0, \pm 1$ . The angular parts of the different terms in  $|\psi_{\text{free}}|^2$  are illustrated in (a) at an arbitrary particular radius by projecting them onto the surface of a sphere. The  $\ell = 1, m = 0$  initial state gives rise to three terms. The cross term, containing the product of the renormalized spherical harmonics  $Y_{0,0}$ and  $Y_{2,0}$  (see the text for details), represents interference of the s and d free-electron waves. When all possible I<sup>-</sup> detachment channels are combined, (b), it is clear that the corresponding free-electron radial functions must be considered to explain the observed photoelectron angular distribution. The correct distribution is predicted (c) when we account for the  $\pi/2$  phase shift of the d and s waves.

these in the manner of eqn (9) yields the overall angular distributions in Fig. 5(b) and (c). Fig. 5(b) illustrates the case of a positive contribution from the cross term, while 5(c) shows the situation for  $R_0$  and  $R_2$  having opposite signs. Only the latter case is in agreement with experiment. In order to understand why this should be, we must briefly consider the nature of the free-electron radial functions.

For simplicity, we cast the discussion in terms of the wavefunctions for the momentum eigenstates. The corresponding solutions of the radial part of the time-independent Schrödinger equation can be expressed as:

$$R_{\ell}(r) = (1/r)D_{\ell}\sin(kr - \ell\pi/2 + \delta_{\ell})$$
(10)

where  $\delta_{\ell}$  is the phase shift of the corresponding partial wave. Physically this arises through interactions of the departing electron with the atomic potential.  $D_{\ell}$  is determined by the cross-section of the corresponding detachment channel. Assuming that the phase shifts  $\delta_0$  and  $\delta_2$  are similar, the  $\ell \pi/2$  phase term is of particular relevance. It arises from the centrifugal interaction associated with the orbital angular momentum of the departing electron and means that the radial components of the  $\ell = 0$  and  $\ell = 2$  partial waves have *opposite* signs. It is interesting to note at this point that, while the sine term oscillates rapidly with wavenumber k, for a given k the s and d partial waves will always be  $\pi$  out of phase according to the arguments above. Hence the above considerations will apply to all eigenfunctions contributing to the wavepacket.

#### 5. Photoelectron imaging of molecular anions

#### 5.1 The effect of molecular energy levels

Molecular anion photoelectron images are inherently more complex than those for atomic anion photodetachment. This is easily seen in photodetachment from  $CS_2^-$ , the results for which are shown in Fig. 6. The 800 nm detachment of the anion yields the corresponding neutral molecule in its ground electronic state. Even with vibrationally cold  $CS_2^-$ , multiple vibrational quanta of the neutral molecule are excited.<sup>16</sup> This (bending) vibrational progression is manifested in the concentric rings in Fig. 6(a). The ground electronic state of the neutral is also accessed upon photodetachment at 267 nm (seen in the outer band of Fig. 6(b)), but the resulting photoelectrons are more energetic. As the energy resolution of velocity-map imaging decreases with increasing eKE, the



Fig. 6  $CS_2^-$ -molecular anion detachment. Photoelectron images resulting from (a) 800 and (b) 267 nm detachment are presented with the raw experimental data on the left hand side and the inverse Abel transformation on the right. Note: the image scales are different for (a) and (b). Transitions are labeled according to the resulting neutral electronic state, assigned based on the known energetic ordering of these states.

vibrational structure is not resolved at 267 nm, though the angular distribution of the outer photoelectron band is clearly polarized along the laser electric vector, as in the 800 nm image. The higher photon energy at 267 nm allows access to several other detachment channels, manifested in the inner image bands in Fig. 6(b). These transitions correspond to detachment from different occupied anion orbitals, yielding the neutral molecule in its first three electronically excited states.

#### 5.2 Angular distributions in molecular anion detachment

In molecular anion photodetachment, the angular distribution once again depends on the contributions of the photoelectron partial waves. In this section, we discuss the relationship between PADs and the corresponding parent molecular orbitals and outline a simple qualitative model relating the parent orbital to the recorded image. As in the atomic anion case, the free-electron wavefunction can be expressed as a combination of partial waves characterized by defined  $\ell$  and *m* quantum numbers. Understanding the relation between these partial waves and the parent molecular orbital is less intuitive than for the atomic case, since  $\ell$  is generally not a good quantum number for molecular orbitals. Nonetheless, the PADs measured for molecular anions bear important information about the parent orbitals, as well as the photodetachment process (see, for example, ref. 23). This is clearly borne out in Fig. 6b, which reveals different PADs for the X, a and b and B transitions in the 267 nm detachment of  $CS_2^{-}$ . The observed differences in the anisotropy parameter  $(X^{1}\Sigma_{g}^{+} \leftarrow X^{2}A_{1}, \beta = +0.27; A^{1}A_{2} \leftarrow X^{2}A_{1}, \beta = -0.44;$  $b^{3}A_{2} \leftarrow X^{2}A_{1}, \beta = -0.42; a^{3}B_{2} \leftarrow X^{2}A_{1}, \beta = -0.24)^{21}$  reflect the markedly different origins of the corresponding photoelectrons.

For molecular anion detachment the link between the measurement frame of reference, *i.e.* the laboratory frame (LF) and the molecule frame (MF) is more complicated than for atomic anion detachment. For atomic anions, the axis of quantization is imposed by the laser polarization, which creates a simple relationship between the LF and the parent anion. In eqn (6) we then only needed to consider the z component of the transition dipole moment. Molecular anions, on the other hand, generally have three distinct axes defined by the structure of the molecule. In principle, the transition dipole moment along each of these axes and the transition intensity is therefore given by:

$$I = (\varepsilon_{\mathbf{p}} M)^{2} = (\varepsilon_{\mathbf{p}} M_{X} + \varepsilon_{\mathbf{p}} M_{Y} + \varepsilon_{\mathbf{p}} M_{Z})^{2}$$
(11)

where M is the transition dipole moment of eqn (5), X, Y, and Z are the molecular-frame axis, while  $\varepsilon_{\mathbf{p}}$  is the laser electric field (polarization) vector, directed along the laboratory frame z axis. For j = X, Y, and Z,  $M_j = \langle \psi_f | \boldsymbol{\mu}_j | \psi_i \rangle$  defines the corresponding components of the transition dipole moment along a given molecular axis, analogous to eqn (6). In an experiment, the molecular anions are randomly oriented with respect to z and therefore  $\varepsilon_{\mathbf{p}}$ . The contribution of  $\varepsilon_{\mathbf{p}}M_j$  to I is proportional to  $\cos^2 \alpha$ , where  $\alpha$  is the angle between the laser polarization axis and  $M_j$ . For the purposes of drawing a connection between a parent orbital and the image it is often

instructive to consider just two or three "principal" orientations of the molecule with respect to  $\epsilon_p$ .

5.2.1 Detachment from the molecule's perspective. We must first consider the detachment process in the MF. The condition of eqn (5) allows determination of the symmetries of the outgoing free-electron waves. Each  $M_i$  has an associated free-electron state  $|\psi_f\rangle$ . The angular momentum wavefunctions (with quantum numbers  $\ell$  and m) associated with this state are spherical harmonics of the same symmetry. To simplify the treatment we follow the approach proposed by Reed et al. (albeit in a different context).<sup>28</sup> Only the waves with the smallest  $\ell$  allowed for each transition are considered and we limit  $\ell$  to a maximum value of 1. These approximations (which are inspired by the Wigner threshold law and therefore best justified for relatively slow photoelectrons) allow insight into the composition of the PAD and its relation to the parent orbital, whilst removing many complications of a rigorous quantitative approach. A more elaborate variant of this approach, termed the s + p model, has been applied to the qualitative interpretation of angular distributions in several benchmark cases.<sup>16</sup>

The  $X^1 \Sigma_g^+ \leftarrow X^2 A_1$  channel of  $CS_2^-$  photodetachment serves as an example. The bent equilibrium structure of  $CS_2^-$  belongs to the  $C_{2v}$  symmetry point group and the  $X^1 \Sigma_g^+ \leftarrow X^2 A_1$  photodetachment transition corresponds to electron ejection from a molecular orbital of  $a_1$  symmetry. The symmetry product associated with  $\langle \psi_f | \boldsymbol{\mu}_j | \psi_i \rangle$  must contain the totally symmetric representation of the  $C_{2v}$  point group for the transition dipole to be non-zero. Thus,  $\Gamma(\psi_f) =$  $\Gamma(\boldsymbol{\mu}_j) \otimes a_1$ .  $\Gamma(\boldsymbol{\mu}_j)$  is equivalent to that of the appropriate MF axis, X, Y, or Z. From the  $C_{2v}$  character table,  $\Gamma(\boldsymbol{\mu}_X) = b_1$ ,  $\Gamma(\boldsymbol{\mu}_Y) = b_2$ ,  $\Gamma(\boldsymbol{\mu}_Z) = a_1$ . Therefore in the MF the X, Y, and Z transition dipole components yield  $\Gamma(\psi_f) = b_1$ ,  $b_2$ , and  $a_1$ , respectively. Further reference to the  $C_{2v}$  character table shows that s and  $p_Z$  waves correspond to  $a_1$  symmetry, whilst  $p_X$  and  $p_Y$  correspond to  $b_1$  and  $b_2$ , respectively.

**5.2.2** The lab-frame perspective. In principle, partial waves produced from all three components of M contribute to the recorded LF PAD. A particular component makes its maximum contribution when it is parallel to the laser polarization axis ( $\alpha = 0$ ). This allows us to make a simple qualitative link between the LF and MF. For example, when the MF Z axis is parallel to the LF z axis these directions are equivalent and a MF  $p_Z$  wave will be polarized along the LF z axis. However, if the MF X axis is parallel to the LF z axis, a MF  $p_X$  wave will be polarized parallel to the LF z axis. For the  $X^1\Sigma_g^+ \leftarrow X^2A_1$  transition the dominant wave contributions are either isotropic or have intensities that peak parallel to the laser polarization vector. The smallest- $\ell$  partial waves (either s or p) allowed for each relative orientation are illustrated as follows:



**Table 1** Allowed free-electron wave symmetries for molecular anions of  $C_{2v}$  symmetry. For a particular orientation (where *j* is parallel to  $\mathbf{\epsilon}_{\mathbf{p}}$ ), the direct product  $\Gamma(\boldsymbol{\mu}_j) \otimes \Gamma(\boldsymbol{\psi}_i)$  is found in the column labeled MF. Alongside are shown the MF partial waves to which this corresponds. The LF column shows the LF polarization of the MF partial waves for a given orientation. The symbols  $\bot$ ,  $\parallel$  and  $\bigcirc$  denote perpendicular polarization, parallel polarization, and isotropic probability density, respectively. The  $a_2$  irreducible symmetry representation does not conform to any spherical harmonic with  $\ell \leq 1$ 

$C_{2v}$	$\Gamma(\psi_{\rm i}) = a_1$		$\Gamma(\psi_{\rm i}) = a_2$		$\Gamma(\psi_{\rm i}) = b_1$		$\Gamma(\psi_i) = b_2$	
$\Gamma(\boldsymbol{\mu}_X) = b_1$ $\Gamma(\boldsymbol{\mu}_Y) = b_2$ $\Gamma(\boldsymbol{\mu}_Z) = a_1$	$ \begin{aligned} \mathbf{MF} \\ b_1 &\equiv \mathbf{p}_X \\ b_2 &\equiv \mathbf{p}_Y \\ a_1 &\equiv \mathbf{s} + \mathbf{p}_Z \end{aligned} $	LF       	$MF  b_2 \equiv p_Y  b_1 \equiv p_X  a_2$	LF ⊥ ⊥	$MF  a_1 \equiv s + p_Z  a_2  b_1 \equiv p_X$	LF ○, ⊥ ⊥	$MF a_2 a_1 \equiv s + p_z b_2 \equiv p_Y$	LF  _⊥

The positive  $\beta$  obtained for the  $X^1\Sigma_g^+ \leftarrow X^2A_1$  transition corresponds to a parallel electron distribution, in accordance with the expectations of even this approach. Table 1 summarizes the predictions for detachment from all possible orbital symmetries of  $C_{2v}$  molecules. Comparing with the  $\beta$  values extracted from Fig. 6, the reader should be aware that the parent electronic state label is not necessarily the same as that of the detachment orbital symmetry. The  $A^1A_2 \leftarrow X^2A_1$  and  $b^3A_2 \leftarrow X^2A_1$  transitions occur from an  $a_2$  orbital and the prediction is that the distribution should be perpendicularly polarized. Similarly the  $a^3B_2 \leftarrow X^2A_1$  transition, in which the detachment orbital has  $b_2$  symmetry, is predicted to have a perpendicular electron distribution. These predictions are in agreement with the negative  $\beta$  determined for these transitions.

The above analysis allows for an important generalization. The outgoing electron waves emitted from a totally symmetric parent orbital must generally belong to the same symmetry species as the active component of the dipole moment. Therefore, regardless of the molecular point group, we expect photodetachment from any totally symmetric parent orbital to be characterized by a predominantly parallel photoelectron distribution. We see this effect in the H<sup>-</sup> and CS<sub>2</sub><sup>-</sup> (the  $X^1 \Sigma_{\sigma}^+ \leftarrow X^2 A_1$  transition) images. Although the parent orbitals in these two cases are very different (an atomic 1s orbital vs. a molecular orbital with several nodes composed of three p atomic orbitals), both result in predominantly parallel photoelectron angular distributions (see Fig. 2 and 6). This general rule has important implications to other anion systems, as well as clusters. For example, in the photodetachment from broadly delocalized s-type states (such as, for example, the hydrated electron states)<sup>29</sup> we *a priori* expect a positive photoelectron anisotropy.

The above arguments are qualitative in nature and therefore not suitable for a rigorous interpretation of the PADs. For example, the model makes no attempt to account for the variations in the partial wave cross-sections and relative phases, as well as the contribution of  $\ell > 1$  partial waves. Herein lie the quantitative differences in the H<sup>-</sup> and CS<sub>2</sub><sup>-</sup>  $(X^{1}\Sigma_{g}^{+} \leftarrow X^{2}A_{1})$  anisotropy parameters. Our purpose has been to show how the imaging technique is able to reveal details of electronic structure.

As a final, and particularly striking, example we make brief mention of imaging studies of photodetachment from the HOMO of the covalently bound dimer anions of  $CS_2$  and  $CO_2$ . The lowest-energy detachment transition of  $(CS_2)_2^$ yields a perpendicular PAD, whilst that of  $(CO_2)_2^-$  has a strongly parallel PAD. The origin of this difference is in the parent anion electronic structure, despite the isovalence of these two species. The  $(CO_2)_2^{-}$  anion is predicted to have either  $D_{2d}$  or  $D_{2h}$  symmetry depending on the level of theoretical treatment applied. However, in either case the HOMO symmetry is that of the totally symmetric representation of these point groups. In the case of  $(CS_2)_2^{-}$ , theoretical treatments predict the structure is different (the molecular symmetry is  $C_{2v}$ ) and more pertinently the HOMO does conform to the totally symmetric representation of the symmetry group. This difference is clearly revealed in the experimental photoelectron images reported in ref. 30. Anisotropy parameter values of opposite signs are obtained in detachment from the HOMO of these two species.

We have presented an introduction to the concepts important to understanding the relationship between a photoelectron image and the parent orbital using examples of anion photodetachment. The photoelectron imaging approach to studies of molecular structure and dynamics is finding increasing application, and rigorous theoretical treatments of photoelectron angular distributions at increasing levels of sophistication are being developed (see, for example, ref. 14 and the references therein). However, we believe that the qualitative approach outlined here highlights perhaps the most important conclusion from the reported studies: that photoelectron imaging can indeed provide decipherable and distinguishable signatures of the parent molecular orbitals.

It is important to bear in mind that the relationship between the image and parent orbital is governed by details of the electron ejection process. For anion photodetachment the dominant long range interaction is centrifugal leading to an energy barrier to detachment proportional to the angular momentum of the departing electron. In the case of photoionization, the coulombic attraction between the departing electron and residual cation dominates and it may no longer be appropriate to ignore  $\ell > 1$  partial waves for neutral ionization. This will alter the contributing partial waves in the free-electron wavefunction. However, the key point identified here is still valid for both anion and neutral systems; a photoelectron image represents a signature of the parent orbital.

Setting anion photoelectron imaging in a wider context, information on electronic state symmetry can also be obtained from UV spectroscopy of neutral molecules, although the range of accessible states is generally limited by spectroscopic selection rules. In contrast, negative-ion experiments provide access to neutral states of different multiplicity, as seen, for example, in Fig. 6 for  $CS_2$ . This important advantage comes in addition to providing a unique perspective of the anions themselves.

#### 6. Summary

Photoelectron imaging is a powerful and increasingly widespread research tool for the study of electronic structure and molecular level details of reaction dynamics. Photoelectron images represent an accumulated series of electron impacts on a position-sensitive detector whose pattern reflects the free-electron probability distribution, the square modulus of the free-electron wavefunction.

We have introduced the concepts central to an understanding of photoelectron imaging and image interpretation, outlining relatively simple qualitative arguments to explain the nature of the PAD. These models rely on properties of the free-electron wavefunction, which in turn are dependent on the originating orbital. Several different, but essentially equivalent, approaches to the interpretation of images resulting from the detachment of atomic anions are available. In particular, consideration of partial wave interference is necessary to properly understand the PADs in all but the simplest cases. As the photoelectrons are detected in the asymptotic limit, one might think that interference should be considered solely in terms of the angular part of the wavefunctions contributing to the freeelectron wavepacket. However, the *l*-dependent electron-neutral interactions experienced in the early stages of detachment determine the asymptotic contribution of the radial part of the wavefunction and hence the overall interference pattern. The centrifugal phase term in the radial wavefunction (as discussed for I<sup>-</sup>) is particularly significant in this regard.

Whilst the atomic anion detachment process is principally discussed from the point of view of electron orbital angular momentum, we also introduced an equivalent approach based on symmetry selection rules. Using what might seem like drastic approximations, it is nevertheless possible to use the symmetry based formalism to interpret molecular anion photoelectron images. Even the purely qualitative approach outlined here helps obtain striking insights into molecular electronic structure.

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# References

- 1 D. W. Chandler and P. L. Houston, J. Chem. Phys., 1987, 87, 1445.
- 2 A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.*, 1997, **68**, 3477.
- 3 M. S. Elioff, J. J. Valentini and D. W. Chandler, *Science*, 2003, **302**, 1940.
- 4 S. M. Sheehan, B. F. Parsons, J. Zhou, E. Garand, T. A. Yen, D. T. Moore and D. M. Neumark, *J. Chem. Phys.*, 2008, **128**, 034301.
- 5 S. J. Cavanagh, S. T. Gibson, M. N. Gale, C. J. Dedman, E. H. Roberts and B. R. Lewis, *Phys. Rev. A*, 2007, **76**, 052708.
- 6 M. A. Sobhy and A. W. Castleman, J. Chem. Phys., 2007, 126, 154314.
- 7 M. S. Bowen and R. E. Continetti, J. Phys. Chem. A, 2004, 108, 7827.
- 8 R. Mabbs and A. Sanov, Int. Rev. Phys. Chem., 2008, 27, 53.
- 9 F. Pagliarulo, B. Climen, B. Baguenard, F. Lepine, M. A. Lebeault, A. Ollagnier, J. Wills and C. Bordas, *Int. J. Mass Spectrom.*, 2006, 252, 100.
- 10 A. Kammrath, G. B. Griffin, J. R. R. Verlet, R. Young and D. M. Neumark, J. Chem. Phys., 2007, 126, 244306.
- 11 T. Suzuki, Annu. Rev. Phys. Chem., 2006, 57, 555.
- 12 I. V. Hertel and W. Radloff, Rep. Prog. Phys., 2006, 69, 1897.
- 13 B. Baguenard, J. C. Pinare, C. Bordas and M. Broyer, *Phys. Rev.* A, 2001, **63**, 023204.
- 14 C. M. Oana and A. I. Krylov, J. Chem. Phys., 2007, 127, 234106.
- 15 T. Seideman, Annu. Rev. Phys. Chem., 2002, 53, 41.
- 16 E. Surber, R. Mabbs and A. Sanov, J. Phys. Chem. A, 2003, 107, 8215.
- 17 D. H. Parker and A. T. J. B. Eppink, J. Chem. Phys., 1997, 107, 2357.
- 18 R. Reichle, H. Helm and I. Y. Kiyan, Phys. Rev. A, 2003, 68, 063404.
- 19 R. Mabbs, E. Surber and A. Sanov, J. Chem. Phys., 2005, 122, 0543081.
- 20 R. N. Zare, Mol. Photochem., 1972, 4, 1.
- 21 R. Mabbs, E. Surber and A. Sanov, Analyst, 2003, 128, 765.
- 22 K. M. Ervin and W. C. Lineberger, in *Advances in Gas Phase Ion Chemistry*, ed. N. G. Adams and L. M. Babcock, JAI Press, Greenwich, 1992.
- 23 L. Velarde, T. Habteyes, E. R. Grumbling, K. Pichugin and A. Sanov, J. Chem. Phys., 2007, **127**, 084302.
- 24 H. A. Bethe, *Handbuch der Physik*, H. Geiger and W. Scheel, J. Springer, Berlin, 1933, vol. 24, pp. 483–273.
- 25 J. Cooper and R. N. Zare, in *Atomic collision processes*, ed. S. Geltman, K. T. Mahanthappa and W. E. Brittin, Gordon and Breach Scientific Publishers, New York, London, Paris, 1968.
- 26 D. Hanstorp, C. Bengtsson and D. J. Larson, *Phys. Rev. A*, 1989, 40, 670.
- 27 R. Mabbs, K. Pichugin and A. Sanov, J. Chem. Phys., 2005, 123, 054329.
- 28 K. J. Reed, A. H. Zimmerman, H. C. Andersen and J. I. Brauman, J. Chem. Phys., 1976, 64, 1368.
- 29 A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky and D. M. Neumark, *Science*, 2004, **306**, 669.
- 30 R. Mabbs, E. Surber and A. Sanov, Chem. Phys. Lett., 2003, 381, 479.