# Cluster anions: Structure, interactions, and dynamics in the sub-nanoscale regime

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Received 13th January 2004, Accepted 25th February 2004 First published as an Advance Article on the web 17th March 2004

This article reflects on several recent advances in the studies of structure and dynamics of cluster anions, both as unique species and as a conceptual bridge between isolated molecules and the condensed phase. Applications involving photofragment and photodetachment spectroscopy, as well as femtosecond time-resolved experiments, are described. Special emphasis is given to the effects of microscopic solvation on the electronic structure and reactivity of negative ions in heterogeneous and homogeneous cluster environments. Several recent breakthroughs in experimental methodology are outlined, in particular the application of photoelectron imaging to the studies of molecular cluster anions.

### 1. Introduction

Clusters have long fascinated chemists by the unique opportunities they offer for the studies of intermolecular interactions implicated in practically all areas of chemistry. Ionic clusters are especially appealing for experimental studies of reactions, as in their well-defined microscopic environments the chemical dynamics can be examined at an unprecedented, molecular level of detail.<sup>1–4</sup> Such detailed analysis is difficult to achieve in macroscopic media, such as liquids, solids, or high-pressure gases, because of the poorly defined solvent coordination and the large number of pairwise interactions involved. These characteristics of condensed environments usually require an averaged description of bulk properties.

Despite their small size, clusters retain many characteristics of the bulk media that make the condensed-phase dynamics as rich as they are. The multitude of intermolecular interactions in clusters affords chemical reactions a variety of pathways and mechanisms that attracted the interest of many generations of chemists. The origin of the field of cluster chemistry can be traced back to the early studies of colloids, aerosols, and nucleation phenomena in the mid-nineteenth century, followed by an explosive growth during the twentieth century. For decades, many experimental and theoretical studies have been directed at deepening the understanding of reaction mechanisms within clusters. This paper is not intended to offer a comprehensive review of the vast field. Its scope is limited to recent photodissociation and photodetachment studies of cluster anions, giving a somewhat personal perspective of the dynamics of photoinduced reactions in cluster anions and the connections between the 'cluster' and condensed phases from the authors' points of view. A broader outlook on the advances in cluster research during the later part of the twentieth century can be found, for example, in the review by Castleman and Bowen.<sup>1</sup>

This paper builds on our recent *Perspective* article,<sup>5</sup> complementing it with an overview of the most recent developments in the field of cluster anions. We concentrate on a few recent successes in the quest for better understanding of solventinduced effects on the electronic structure and reaction dynamics and discuss the role of solvent-induced perturbations in determining the outcomes of chemical reactions. These perturbations are particularly important in reactions involving non-adiabatic transitions. The interactions implicated in ionic solvation often cannot be considered as merely a 'perturbation', in the perturbation-theory sense. The cumulative ionsolvent interactions in ionic clusters can be easily comparable to chemical bonding, enabling chemical transformations and lending the solvent a major role in determining the reaction outcomes. For example,  $I_2^-$ , one of the most studied ionic chromophores,<sup>6-25</sup> has a bond dissociation energy of 1 eV, compared to a typical solvent binding energy of ~0.2 eV per solvent molecule.<sup>22,26</sup> Clearly, the collective effect of the solvent on  $I_2^-$  cannot be viewed as a minor perturbation even in moderate-size clusters. Thus, although the term 'perturbation' is frequently used in this article, it is often assumed to imply a considerable effect rather than a minor modification of state potentials and their couplings.

Different types of solvent-driven reactions require various degrees of such perturbation. In many cases, the perturbation is large, although the reaction could proceed, in principle, even if it were minimal. One example is the solvent-induced recombination, or caging, of photofragments.<sup>5–7,18,21–54</sup> The fundamental appeal of this process lies in that it involves both the breaking and remaking of chemical bonds, both occurring under the influence of the solvent. The classic  $I_2^-$  caging reactions<sup>6–8,22,46,47,50</sup> evolve on potential energy surfaces correlating with the lower  $I_2^-$  dissociation limit yielding the neutral I fragment in the ground spin-orbit state. In this case, the  $I(^{2}P_{3/2}) + I^{-}$  recombination proceeds via a mechanism<sup>55–57</sup> common for caging in both neutral and ionic, gas and condensed<sup>40,58-60</sup> phase systems. The fragment separation is halted by the solvent that absorbs the translational energy and the fragments then recombine following the conversion at large separation to the ground  $I_2^-$  electronic state. Subsequently, the recombined  $I_2^-$  undergoes vibrational relaxation as the energy is transferred to the solvent.<sup>61-63</sup> Although the  $I_2^-$  electronic structure is greatly perturbed by the solvent,64-66 only modest coupling between electronic states is actually needed, as the states in question are asymptotically degenerate. In this straightforward mechanism, the solvent effects are overwhelming in magnitude compared to the 'probe' used to monitor them (*i.e.*, the caging process). Therefore, it is not surprising that one finds the recombination dynamics not to be overly sensitive to the details of cluster structure.

In other cases, a much larger degree of solvent-induced perturbation of the solute is required for the reaction to be possible in principle. A new type of caging reaction ensues when the  $I_2^-$  cluster core is dissociated via the  $I^*({}^2P_{1/2}) + I^-({}^1S)$  channel.<sup>23,25,67</sup> In this case, a simple reversal of fragment trajectories cannot result in recombination, because none of the  $I^{*}({}^{2}P_{1/2}) + I^{-}({}^{1}S)$  potentials are bound. Nevertheless, caging on the ground electronic state is observed, which requires electronic quenching of  $I^*({}^2P_{1/2})$  to precede the recombination. This crucial transition involves an energy gap of nearly 1 eV and is known to be extremely slow when occurring via radiative or binary collisional energy transfer mechanisms. This caging mechanism is exquisitely sensitive to the details of solvent-shell structure, and illustrates the key role of asymmetric, partial solvation of the ionic chromophore in the recombination dynamics.

Many laboratory tools are available today for the studies of ionic clusters. Among the most basic probes of cluster-ion structure and dynamics are mass-spectroscopy, photoelectron spectroscopy, photofragment spectroscopy, and several relatively new ultrafast pump-probe techniques. The field made a jump towards better-controlled and more comprehensive experimental studies with the introduction in the 1980s of the pulsed cluster-ion techniques,<sup>3</sup> coupled with advances in tandem time-of-flight mass-spectroscopy. Lineberger-type pulsed ion sources, now used in many laboratories around the world, allow the preparation and mass-selection of internally cool ionic clusters of known composition and often predictable structure. Using a combination of photoelectron and photofragment spectroscopic techniques, the reaction dynamics in cluster ions can be studied, revealing the unique physical features of this intriguing species and bridging the gap between the properties of isolated molecules and chemistry and physics of condensed-phase environments.

The next revolutionary experimental tool introduced into the field in the late 1980s and early 1990s is the coupling of ultrafast pump-probe techniques with photoelectron spectroscopy and photofragment measurements. Whereas the experiments in the frequency domain help characterize the chemical and electronic structure of the cluster anions studied, femtosecond pump-probe spectroscopy allows studying the reactions in real time, putting a truly dynamical emphasis on the experiments. The Lineberger group demonstrated the utility of ultrafast photofragment spectroscopy in the studies of cluster ion dynamics,<sup>21,68</sup> while Neumark and co-workers developed a time-resolved variant of negative-ion photoelectron spectroscopy (PES), know as femtosecond PES, which allows the observation of reactions through the window of evolving photoelectron spectra.47 Other trends in the field include the move towards more detailed approaches to photoelectron and photofragment measurements, such as detecting several particles in coincidence,<sup>69-75</sup> spectroscopic characterization of the cluster vibrational modes and structures,  $^{76,77}$  and the imaging  $^{78-80}$  approach to negative-ion PES.  $^{81-87}$ 

In this paper, we discuss several recent benchmark studies of cluster-anion structure and dynamics. Section 2 describes a few structural motifs involved in the cluster-ion formation. Section 3 explores the photofragment caging dynamics, with a special emphasis on the solvent-induced spin–orbit relaxation occurring on a remarkably fast timescale. Section 4 outlines the structural and photochemical effects specific to the homogeneous cluster anions, while Section 5 overviews the recent advances in molecular and cluster anion photoelectron imaging. Finally, Section 6 gives a brief summary and outlines the future directions.

### 2. Structures of heterogeneous cluster anions

The structure of the solvent shell about the ionic core of the cluster plays a determining role in its dynamics. To illustrate the basic principles involved in the shell formation, we discuss the qualitative aspects of building up the first shells of OCS and CO<sub>2</sub> around an I<sub>2</sub><sup>-</sup> core. The structures of I<sub>2</sub><sup>-</sup>(OCS)<sub>n</sub> and I<sub>2</sub><sup>-</sup>(CO<sub>2</sub>)<sub>n</sub> have been examined using molecular dynamics and a model-Hamiltonian approach in a number of publications by the Parson group.<sup>23,36,66,88,89</sup> Their findings are in agreement with a number of experimental observations, some of which are highlighted in the following sections.

In the  $I_2^{-}(OCS)_n$  cluster ions the binding of the solvent is dominated by charge-dipole interactions between  $I_2^{-}$  and OCS, whereas in  $I_2^{-}(CO_2)_n$ , in the absence of a permanent CO<sub>2</sub> dipole moment, the charge-quadrupole interaction takes center stage.<sup>88,90,91</sup> The solvent-solvent interactions also play important roles. Since the charge in unsolvated  $I_2^{-}$  is equally divided between the two I-atoms, electrostatic considerations dictate that in stepwise solvation the first solvent molecule is expected to bind near the waist of  $I_2^{-}$ . Thus, in  $I_2^{-}$ ·OCS the positively charged S-end of the solvent points toward the  $I_2^{-}$ center of mass. In larger  $I_2^{-}(OCS)_n$  clusters, solvent-solvent interactions are added and the above solvent orientation motif is modified to accommodate these interactions.

The most revealing minimum-energy  $I_2^{-}(OCS)_n$  structures determined by the Parson group are shown in Fig. 1.<sup>23</sup> The first five OCS molecules are found to arrange themselves around the waist of  $I_2^{-}$  with the sulfur atoms about 3.6 Å from the  $I_2^{-}$  center of mass. As a result of the solvent-solvent interactions, the OCS are tilted at about 117°, rather than pointing directly outward, as best seen in Fig. 1(a). In  $I_2^{-}(OCS)_5$ , the five OCS molecules complete a ring around  $I_2^{-}$ . The next five form a second ring around one end of the solute, then a single



**Fig. 1** Calculated minimum-energy structures of  $I_2^-(OCS)_n$ , n = 5, 11, and 17. Each structure is shown from two different angles, viewed perpendicular and along the  $I_2^-$  bond (left and right columns, respectively). These structures correspond to the isomers selected out of many nearly isoenergetic solvent configurations. While the general manner of solvent packing around  $I_2^-$  is reproduced in all low-energy isomers, local structural details, such as the relative orientation of neighboring OCS molecules, may vary. Adapted from ref. 23.

OCS molecule fills the axial site, "capping" that end of the cluster and completing the half-shell structure of  $I_2^-(OCS)_{11}$  shown in Fig. 1(b). It is notable that  $I_2^-(OCS)_{11}$  corresponds to a prominent "magic number" in the  $I_2^-(OCS)_n$  cluster mass-spectrum, *i.e.*, the n = 11 peak clearly stands out in intensity compared to its neighbors.<sup>23</sup> This observation supports the particularly stable structure of this cluster predicted by the Parson model. The other side of the  $I_2^-(OCS)_n$  cluster shell is filled in a similar fashion, completing the first solvation shell with 17 OCS molecules [Fig. 1(c)].

In  $I_2^{-}(CO_2)_n$ , the charge-quadrupole interactions with the cluster core result in CO<sub>2</sub> molecules lying flat with respect to  $I_2^{-}$ . Parson and co-workers have shown that the CO<sub>2</sub> molecules tend to first pack together on one side of  $I_2^{-}$ , as shown in Fig. 2 for  $I_2^{-}(CO_2)_5$ ,<sup>37,66,88,92</sup> rather than form a 'ring' [compare the structure of  $I_2^{-}(CO_2)_5$  to  $I_2^{-}(OCS)_5$  in Fig. 1(a)]. This type of packing maximizes the interactions within the CO<sub>2</sub> solvent shell itself. To the contrary, the ring structure of an OCS shell accentuates the strength of solvent-solute interactions, which are the strongest near the solute's waist.

### 3. Photofragment caging dynamics

The photodissociation and recombination of  $I_2^-$  have been studied in both bulk liquids, such as water and alcohols (Barbara and co-workers),<sup>6,7,46</sup> and gas-phase clusters (Lineberger and Neumark groups).<sup>21–26,49–51,54,63,68,93</sup> Kondow and coworkers examined collisions of  $I_2^-(CO_2)_n$  with solid surfaces and observed a wedge-type splitting of the  $I_2^-$  bond by  $CO_2$ molecules upon cluster-surface collisions.<sup>11,12,94,95</sup> The dynamics of ionic clusters have been compared to the studies of  $I_2$  recombination in solid rare-gas matrices by the Apkarian group.<sup>40,58–60</sup> Several groups provided extensive theoretical background on the dissociation and recombination in clusters.<sup>16,17,35,37,66,67,92,96</sup> In the analysis of Parson and co-workers, the photofragmentation and caging are mediated by couplings of electronic states with differential charge character that is caused by interactions with the solvent.<sup>37,48,66,92,97</sup> It was shown that differential solvation of electronic states can lead to isoenergetic curve-crossing regions playing key roles in the relaxation and recombination dynamics.

We provide a perspective of the dynamics involved in caging by considering the photodissociation and recombination of  $I_2^$ in clusters of the OCS<sup>23–25,54</sup> and CO<sub>2</sub><sup>21,22,26,49,50,62,63,68,98,99</sup> solvents. Together with the studies of  $I_2^-$  in N<sub>2</sub>O<sup>93</sup> and Ar,<sup>47,50,51,61</sup> these experiments highlight the structural and dynamical effects of closed-shell solvents with different electrostatic properties.

The original studies<sup>21,22,26,49,50</sup> of I<sub>2</sub><sup>-</sup> in clusters utilized the A'  ${}^{2}\Pi_{g,1/2} \leftarrow X {}^{2}\Sigma_{u,1/2}^{+}$  transition centered near 790 nm to promote the dissociation. This transition, yielding the I<sup>-</sup> + I( ${}^{2}P_{3/2}$ ) asymptotic products, is indicated by a red vertical arrow in Fig. 3, which shows the unperturbed I<sub>2</sub><sup>-</sup> potentials calculated by Parson and co-workers.<sup>92</sup> Later, striking new dynamics<sup>23,25</sup> were observed in the I<sub>2</sub><sup>-</sup>(OCS)<sub>n</sub> and I<sub>2</sub><sup>-</sup>(CO<sub>2</sub>)<sub>n</sub> cluster ions excited at 395 nm *via* the B  ${}^{2}\Sigma_{g,1/2}^{+} \leftarrow X {}^{2}\Sigma_{u,1/2}^{+}$  transition in the I<sub>2</sub><sup>-</sup> chromophore (indicated by a blue arrow in Fig. 4). This



**Fig. 2** Calculated minimum-energy structure of  $I_2^-(CO_2)_5$  as viewed along the axes perpendicular (left) and parallel (right) to the  $I_2^-$  bond. Adapted from ref. 37.



**Fig. 3** Potential energy diagram of  $I_2^-$  (from ref. 92) and solvent loss energetics in 790 nm experiments on  $I_2^-(OCS)_n$  or  $I_2^-(CO_2)_n$ .

excitation accesses an electronic state correlating with the  $I^-+I^*(^2P_{1/2})$  limit, where  $I^*$  indicates a spin–orbit-excited fragment.

The 790 and 395 nm dynamics are quite different. In a qualitative view of the dynamics following the near-IR excitation (Fig. 3), one might consider the solvent playing a dual role. First, it acts as a physical barrier blocking the exit channel for photofragment escape from the cluster, thus triggering recombination. Second, it acts as an energy bath, enabling the relaxation of the caged chromophore and cluster as a whole by evaporation of solvent molecules. The right-hand side of Fig. 3 illustrates the solvent loss energetics involved in the process. As each solvent molecule (OCS or CO<sub>2</sub>) is bound to the cluster by ~0.2–0.25 eV, the complete dissipation of the 790 nm photon energy requires the evaporation of ~6 solvent molecules. Alternatively, if the  $I_2^-$  bond is not reformed, only two or three solvent molecules are lost by the  $I^-(OCS)_k$  fragments in the uncaged channel.

Although the true mechanism is more complex,<sup>37,66,88,96</sup> this simplified picture does provide an initial understanding of the dynamics. The seeming simplicity stems from the lack of consideration given to the solvent-induced perturbation of the  $I_2^$ electronic structure. However, little perturbation is actually needed to envision the recombination process in this case. The only perturbation required is that which would enable transitions from the bright  $I_2^-$  state back to the ground electronic state, on which the recombination process ultimately terminates. Given that the A' state as well as two other excited states (A and a) are asymptotically degenerate with the X state, the required transitions can occur in the exit channel with a minimum solvent-induced perturbation providing the state



**Fig. 4** Potential energy diagram of  $I_2^-$  (from ref. 92) and solvent loss energetics in 395 nm experiments on  $I_2^-(OCS)_n$  or  $I_2^-(CO_2)_n$ .

coupling. Thus, one obtains a tutorial picture of the reaction by considering the dissociation of largely unperturbed  $I_2^-$  confined inside the solvent cage.

The situation is dramatically different at 395 nm (Fig. 4). The B  ${}^{2}\Sigma_{g,1/2}^{+} \leftarrow X \, {}^{2}\Sigma_{u,1/2}^{+}$  transition in bare I<sub>2</sub><sup>-</sup> leads to dissociation exclusively on the spin-orbit excited I<sup>-</sup> + I\*( ${}^{2}P_{1/2}$ ) asymptote with a translational energy release of about 1.2 eV. No products are formed on the lower I<sup>-</sup> + I( ${}^{2}P_{3/2}$ ) asymptote.<sup>25</sup> Thus, given the negligible probability of collisional quenching of I\* ( $\sim 10^{-7}$ - $10^{-8}$  per collision),<sup>100</sup> the unperturbed state diagram in Fig. 4 predicts that no I<sub>2</sub><sup>-</sup> caging is possible following the near-UV excitation. The experiment, however, testifies to the contrary,<sup>23,25</sup> raising the main question: Given the highly inefficient quenching of I\* in collisions, how do the I<sup>-</sup> + I\*( ${}^{2}P_{1/2}$ ) fragments find their way to the lower spin-orbit asymptote, on which not only the recombination, but also the uncaged channel B (see Fig. 4) evolve?

The quenching of spin–orbit excitation was found to be surprisingly efficient in the  $I_2^{-}(OCS)_n$  and  $I_2^{-}(CO_2)_n$  cluster ions. In general, three distinct pathways are observed (as labeled in Fig. 4): (A) the "uncaged"  $I^{-}(OCS)_k$  products formed in coincidence with the excited  $I^*(^2P_{1/2})$  fragments, which is ejected from the cluster; (B) the "uncaged"  $I^{-}(OCS)_k$  products formed in coincidence with the quenched  $I(^2P_{3/2})$  fragments; and (C) the "caged"  $I_2^{-}(OCS)_k$  products.

The critical step in channels B and C is the quenching of the spin–orbit excitation. The competition between channels A, B, and C is a delicate probe of the solvent-induced couplings between electronic states, which make the spin–orbit relaxation possible. In all three channels, the excess energy is removed from the cluster by ejecting (n - k) solvent molecules. Additionally, in channel A almost 1 eV is carried away in the form of I\* spin–orbit excitation. As a result, the size distribution of the uncaged I<sup>-</sup>(OCS)<sub>k</sub> products is in general bimodal, compared to a single-modal distribution of the caged I<sub>2</sub><sup>-</sup>(OCS)<sub>k</sub> fragments.<sup>23,25</sup> The typical number of solvent molecules evaporated in each channel is indicated on the right-hand side of Fig. 4.

We continue our discussion of the dynamics in clusters by considering the cluster size-dependent caging probabilities. This is followed by femtosecond pump-probe experiments monitoring the time-resolved dynamics of caging.

### Caging probabilities and their structural implications

First, consider the fraction of caged fragments observed in 790 nm dissociation of  $I_2^{-}(OCS)_n$ . This fraction, referred to as the caging probability, is plotted in Fig. 5 as a function of the number of solvent molecules.<sup>23</sup> No caged products are observed for clusters with n < 3, while for larger clusters the caging probability increases nearly monotonically with n, until



**Fig. 5** Probabilities of recombination (caging) of the  $I_2^-$  chromophore in  $I_2^-(CO_2)_n$  and  $I_2^-(OCS)_n$  clusters following photoexcitation at 790 nm, as functions of the parent cluster size. Data from refs. 23 and 25.

a 100% caging is observed for  $n \ge 17$ . The theoretical simulations described in Section 2 predict that 17 OCS molecules comprise a complete solvent shell around  $I_2^-$  [Fig. 1(c)]. This is consistent with the experimental observation that  $I_2^-$ (OCS)<sub>17</sub> is the smallest cluster anion with the OCS solvent for which a 100% recombination of the chromophore is observed.

Despite the different nature of the dominant interactions in  $I_2^{-}(OCS)_n$  and  $I_2^{-}(CO_2)_n$ , the 790 nm results for  $I_2^{-}(CO_2)_n$ , also shown in Fig. 5,<sup>50</sup> are disappointingly similar to the findings for  $I_2^{-}(COS)_n$ . Complete 790 nm caging in  $I_2^{-}(CO_2)_n$  is observed for  $n \ge 16$ , consistent with the first solvent shell closing at n = 16–17, as predicted by the Monte Carlo simulations.<sup>66,88</sup>

The monotonic increase in 790 nm caging probability and the lack of significant differences between the OCS and CO<sub>2</sub> solvents are consistent with the picture of caging given in the introduction to this Section. Even small perturbations would be sufficient to couple the asymptotically degenerate  $I_2^-$  states, correlating to the lower dissociation limit. Therefore, the intricate details of the interactions are not too important. The main role of the solvent in this case indeed appears to be that of a physical obstacle in the exit channel of  $I_2^-$  dissociation and an energy bath. In this light, increasing the number of solvents bound to the chromophore naturally results in a monotonic increase in the caging probability.

Now consider the entirely different dynamics observed in the 395 nm experiment. The corresponding fraction of the caged fragments is plotted in Fig. 6(a) for both  $I_2^{-}(OCS)_n$  and  $I_2^{-}(CO_2)_n$ .<sup>23,25</sup> As expected, the onset of 395 nm caging takes more solvent molecules compared to 790 nm. However, the caging probability is no longer the only parameter characterizing the channel competition. From a dynamical viewpoint, perhaps of even greater interest is the probability of spin–orbit relaxation induced by the solvent. Regarding the diagram in



**Fig. 6** (a) Probabilities of recombination (caging) of the  $I_2^-$  chromophore in  $I_2^-(CO_2)_n$  and  $I_2^-(OCS)_n$  clusters following photoexcitation at 395 nm, as functions of the parent cluster size. (b) Similar curves for the probability of I\* spin–orbit quenching. Data from refs. 23 and 25.

Fig. 4, the spin-orbit relaxation is prerequisite for channels B and C. The probability of quenching is given by combining the branching ratios for the spin-orbit relaxed uncaged channel B and the caged channel C. Thus obtained probability is plotted in Fig. 6(b) for both  $I_2^-(OCS)_n$  and  $I_2^-(CO_2)_n$  as a function of *n*.

The complete caging is not achieved for any of the parent clusters studied (*e.g.*, up to 26 solvent OCS molecules, for which the caging probability is 0.98). Still, recombination is the dominant reaction pathway for clusters with  $n \ge 17$ . What really sets the 395 nm caging probability curves [Fig. 6(a)] aside from the corresponding 790 nm curves (Fig. 5) is their structured nature. The 395 nm caging curve for the CO<sub>2</sub> solvent is not monotonic in the range of n = 11-16, while the corresponding curve for the  $I_2^-(OCS)_n$  cluster ions exhibits a plateau in the same approximate range (n = 12-16), followed by a step-like nearly three-fold increase at n = 17. Notably, n = 17 is the smallest  $I_2^-(OCS)_n$  cluster size for which 100% caging is observed at 790 nm and it corresponds to a cluster with a predicted complete solvent shell.

The sharp increase in caging upon addition of the 17th OCS molecule is attributed to a steric effect: the 17th molecule occupies the only remaining open site at the end of  $I_2^-$  [see Fig. 1(c)]. The occupation of this site closes the last free escape route for  $I_2^-$  dissociation fragment. The presence of solvent on the  $I_2^-$  dissociation coordinate also increases the likelihood of non-adiabatic quenching of I\*, which is prerequisite for recombination.

Another prominent feature of the  $I_2^{-}(OCS)_n$  caging and spin-orbit quenching probability curves in Fig. 6 is the plateau at n = 12-16. No such plateau is observed for  $I_2^{-}(CO_2)_n$ , for which both caging and quenching in the same cluster size range exhibit seemingly erratic behaviors. It is revealing that the  $I_2^{-}(OCS)_n$  plateau consists of exactly *five* cluster sizes, reminiscent of the theoretical prediction that the first OCS solvent shell around  $I_2^{-}$  consists of three *five*-membered OCS rings plus two end molecules "capping" the cluster (Fig. 1). The plateau thus corresponds to the formation of the third solvent ring around the chromophore. The lack of a similar plateau for  $I_2^{-}(CO_2)_n$  is consistent with the qualitatively different structural motif of  $I_2^{-}(CO_2)_n$ , which is not based on solvent rings (see Fig. 2).

The suggested mechanism of the spin–orbit quenching and recombination is discussed following the examination of the timescales on which these processes transpire.

### Time-resolved dynamics of caging

The application of time-resolved techniques to chemical processes occurring on sub-picosecond timescales has been one of the most important developments in reaction dynamics during the past decade.<sup>47,79,101–107</sup> In particular, the application of femtosecond pump–probe spectroscopy to cluster anions allowed the examination of the relaxation and energy-transfer processes at unprecedented levels of detail.

The dissociation of the I<sub>2</sub><sup>-</sup> chromophore within a cluster destroys the cluster's ability to absorb visible/near-IR light, resulting in transient bleaching. As the ensuing recombination revives the absorption cross-section, a second photon can probe either the A'  ${}^{2}\Pi_{g,1/2} \leftarrow X {}^{2}\Sigma_{u,1/2}^{+}$  or the a  ${}^{2}\Pi_{u,3/2} \leftarrow A {}^{2}\Pi_{g,3/2}$  transition.<sup>22</sup> The absorption recovery provides a way of examining the real-time dynamics of caging by monitoring the delay-dependent yield of two-photon products in a pump–probe experiment. Such measurements using a 720–790 nm pump and probe were performed (among others)<sup>22,50,93</sup> on I<sub>2</sub><sup>-</sup>(CO2)<sub>n</sub> and I<sub>2</sub><sup>-</sup>(OCS)<sub>n</sub> cluster ions.<sup>22,24,25,50,54</sup> The experiments revealed picosecond timescales of the recombination and subsequent relaxation.

Fig. 7(a) shows the absorption recovery curves for  $I_2^{-}(OCS)_7$  and  $I_2^{-}(OCS)_{17}$  obtained in the 790 nm pumpprobe experiments.<sup>25</sup> In this case, the positive and negative



**Fig.** 7 Delay-dependent absorption recoveries of indicated  $I_2^{-}(OCS)_n$  cluster ions following the excitation at (a) 790 nm and (b) 395 nm. In (b), the relaxation processes leading to  $I_2^{-}$  caging include the spin–orbit relaxation of I\*, while in (a) the spin–orbit relaxation step is not involved. Adapted from ref. 25.

delays correspond to the reversal of the order of the identical pump and probe photons and therefore convey the same dynamical information. The near disappearance of the signal at a zero delay reflects the bleaching of probe absorption due to the dissociation of the chromophore by the pump photon. The fast ( $\sim 2$  ps) rise is absorption recovery following 790 nm excitation of I2-(OCS)17 is attributed to the initial recombination of the  $I({}^{2}P_{3/2}) + I^{-}$  fragments. In this delay range, the probe photon is absorbed by  $I_2^-$  in one of the excited electronic states or a highly excited vibrational level of the ground state.<sup>49,96</sup> The 2 ps timescale corresponds to the period of the pseudo-vibrational  $I \cdots I^-$  motion n the system excited above its dissociation threshold but constrained by the solvent. The bump appearing in the  $I_2^{-}(OCS)_{17}$  absorption recovery curve at 2 ps is characteristic of the coherent  $I\cdots I^-\mbox{ motion}^{24,49}$ within the cluster. In  $I_2^{-}(OCS)_7$  the solvent cage is smaller and weaker, the dynamics are correspondingly slower and less coherent, hence the 2 ps peak does not appear. The longer timescale dynamics in both  $I_2^{-}(OCS)_7$  and  $I_2^{-}(OCS)_{17}$ , characterized by the pump-probe signal leveling off after  $\sim 20$  ps, reflect the internal relaxation of the caged I2<sup>-</sup>.

An alternative perspective of these dynamics is provided by time-resolved photoelectron spectroscopy. While the photo-fragment measurements, by their definition, focus primarily on the nuclear degrees of freedom, Neumark and co-workers pioneered an experimental approach that shifts the emphasis to the evolving electronic structure.<sup>47</sup> Femtosecond photoelectron spectroscopy of cluster anions is used to probe the transient states and changing environment of the chromophore or its fragments by recording transient spectra of the electrons detached from the excited cluster with a delayed UV probe pulse.

When these measurements are carried out on isolated  $I_2^-$ , the time-dependent photoelectron spectra reflect the timescale

of the dissociation process.<sup>18–20,108</sup> In the experiments on I<sub>2</sub><sup>-</sup> embedded in Ar or CO<sub>2</sub> clusters,<sup>47,61,62</sup> the transient spectra reveal that after the charge localizes on one of the chromophore fragments, the photoelectron bands exhibit a varying energetic shift due to interactions with the solvent. In small (*e.g.*, *n* = 6) Ar clusters, this shift persists for ~1 ps, which is the time required for I<sup>-</sup> to escape from the cluster.<sup>47</sup> The Parson group's molecular dynamics calculations predicted shifts in electron affinity of the cluster that agree well with Neumark's measurements.<sup>48,97</sup> In larger clusters, the transient photoelectron spectra reveal the recombination of I<sub>2</sub><sup>-</sup> in both ground and excited electronic states, followed by vibrational relaxation and solvent evaporation.<sup>61–63</sup> The timescale of these processes are consistent with the timescales of caging observed by Lineberger and co-workers.<sup>26,50</sup>

To summarize, the fast rise in the  $I_2^{-}(OCS)_{17}$  absorption recovery signal seen in Fig. 7(a) during the first couple of picoseconds reflects the timescale for  $I_2^{-}$  recombination on the lower dissociation asymptote. This timescale is typical of  $I_2^{-}$ recombination in molecular solvents (CO<sub>2</sub>, N<sub>2</sub>O, OCS). Thus, it takes ~2 ps for the solvent shell to reverse the I<sup>-</sup> + I dissociation trajectories and direct the fragments towards recombination.

Similar measurements carried out with a 395 nm pump examined the dynamics on the upper spin–orbit asymptote of the dissociating  $I_2^-$ . The qualitative zeroth-order picture of this process is shown in Fig. 4. The recovery curves for  $I_2^-(OCS)_{17}$  and  $I_2^-(OCS)_{24}$  in Fig. 7(b) reflect the cumulative timescales of spin–orbit relaxation and recombination. For  $I_2^-(OCS)_{24}$ , the initial rise in absorption recovery occurs on a timescale of ~2 ps, similar to the period of solvent-induced coherent  $I \cdots I^-$  motion observed following 720 or 790 nm excitation.<sup>22,24,25,49,50</sup> In the smaller  $I_2^-(OCS)_{17}$  cluster, the recovery is slower, similar to the 720–790 nm results for smaller clusters.

To emphasize this analogy, compare the absorption recovery curves in Figs. 7(a) and (b). The cluster sizes in (a) and (b) are purposefully different, as they were selected for the similarity of the respective timescales. (Qualitatively, adding extra solvent molecules counter balances the effect of doubling the energy pumped into the cluster at 395 nm, compared to 790 nm.) Despite the differences in detail, the timescales of caging following 395 and 790 nm excitations are similar, indicating that the spin–orbit relaxation step implicated in Fig. 7(b), but not in Fig. 7(a), must be fast on the overall timescale of the reaction.

### Solvent-mediated charge transfer as a spin-orbit quenching mechanism

The analysis of 395 nm caging dynamics by the Lineberger and Parson groups shows<sup>23,25,67</sup> that the quenching of spin–orbit excitation enabling the  $I_2^-$  recombination is only possible because of the strong perturbation of the  $I_2^-$  electronic structure by the solvent. Mechanisms failing to consider explicitly the perturbed potentials (*e.g.*, radiative decay or collisional quenching) have been ruled out based on experimental and theoretical evidence.<sup>25</sup> Here, we outline the solvent-asymmetry mediated electron transfer model, first suggested by Maslen *et al.*<sup>64</sup> and developed by Delaney *et al.*,<sup>67</sup> that is accepted as an accurate view of the reaction.

The drawback of the collisional mechanism of I<sup>\*</sup> quenching is that it considers the I<sup>-</sup> fragment as a mere spectator. This strategy fails in the cluster ion environment. As another clue calling for a different approach, I<sup>\*</sup> quenching on a picosecond timescale has not been observed in neutral environments. Thus, the proximity of I<sup>-</sup> is key to understanding the relaxation mechanism.

The energy gap between the two spin-orbit asymptotes in Fig. 4 can be bridged by the effects of solvation. Because of

the substantial binding energy of OCS and  $CO_2$  to a negatively charged cluster (~0.2 eV per molecule), <sup>22,23,26</sup> the relative electronic state energies are greatly affected by the state-specific charge distributions and solvent asymmetry. In the example in Fig. 8, the asymptotic  $I^- + I({}^2P_{3/2})$  and  $I^- + I^*({}^2P_{1/2})$  states are separated by 0.93 eV in the unsolvated  $I \cdots I^-$  system (Fig. 8, top left). These states are degenerate with respect to switching the fragment positions  $(I^- + I \text{ versus } I + I^- \text{ and } I^- + I^* \text{ ver-}$ sus  $I^* + I^-$ ). In the cluster environment, the degeneracy is lifted by asymmetric solvation of the fragment pair (Fig. 8, top right). If the charge is localized at the more solvated end (*i.e.*,  $X \cdot I^{-} \cdots I$ , where X denotes the collective solvent), the corresponding state energy is lowered significantly. On the other hand, if the charge resides on the least solvated end  $(X \cdot I \cdot \cdot \cdot I^{-})$ , the solvation effect is less significant. If the energetic difference between the two charge-solvent configurations, termed the differential solvation energy ( $\Delta \Phi$ ), is close to 0.93 eV, the  $X \cdot I^- \cdots I^*$  and  $X \cdot I \cdots I^-$  states may come into resonance, enabling a fast spin-orbit quenching transition by an electron hoping from  $I^-$  to  $I^*$ .

Parson and co-workers developed this picture and identified the electronic states of  $I_2^-$  of different charge-switching character.<sup>64–66</sup> The behavior of these states under differential solvation is illustrated qualitatively in Fig. 8 (bottom). In the



Fig. 8 Top: A qualitative energy diagram illustrating the mechanism of spin-orbit relaxation by solvent-mediated electron transfer from I<sup>-</sup> to I<sup>\*</sup> in an asymmetrically solvated cluster. The required resonance of the X·I<sup>-</sup>···I<sup>\*</sup> and X·I···I<sup>-</sup> electronic states occurs when the differential solvation energy ( $\Delta \Phi$ ) is equal to the spin-orbit energy gap in the I atom (0.93 eV). Bottom left: A qualitative I<sub>2</sub><sup>-</sup> potential energy diagram (unsolvated anion). Bottom left: A qualitative illustration of the behavior of "normal" and "anomalous" charge-switching states of I<sub>2</sub><sup>-</sup> under the conditions of asymmetric solvation. The curve-crossings promote the X·I<sup>-</sup>···I<sup>\*</sup> → X·I···I<sup>-</sup> electron-transfer transitions, quenching the spin-orbit excitation of the I fragment.

states with normal character, the charge gravitates towards the more solvated end of  $I_2^-$ . Compared to unsolvated  $I_2^-$ , the energy of these states decreases with increasing  $I-I^-$  separation due to more efficient solvation as the charge becomes more localized. To the contrary, the anomalous charge-switching states exhibit a charge distribution favoring the least solvated end of the chromophore. The energy of these states increases in dissociation, as the  $I^-$ -solvent interaction drops with increasing  $I-I^-$  distance. The resulting curve-crossings, indicated in Fig. 8 (bottom right), enable an  $X \cdot I^- \cdots I^* \rightarrow X \cdot I \cdots I^-$  transition. Following that, the electrostatic attraction between the solvent and  $I^-$  will tend to reverse the dissociation trajectory towards  $I_2^-$  recombination.

Fig. 8 is only a qualitative illustration with the number and configuration of solvent molecules chosen arbitrarily to satisfy the  $\Delta \Phi \approx 0.93$  eV requirement. In reality, transient resonances between different electron-transfer states are possible starting from a wide range of initial solvent configurations, including nearly symmetric ones. As the cluster breaks up and the charge localizes on one of the fragments, the initial symmetry, if any, is always destroyed and as long as the number of solvent molecules in the cluster is sufficient, the required curve crossing is possible at some transient cluster geometry.

The dynamics on the ground spin-orbit asymptote following the spin-orbit relaxation are reflected in the relative yields of channels B and C (defined in Fig. 4). In the 790 nm experiment, all dynamics transpire on this asymptote, and in small clusters the dissociation is naturally favored over recombination.<sup>23,26,50,93</sup> To the contrary, at 395 nm no preference is observed for  $I^- + I({}^2P_{3/2})$  dissociation over the recombination, even in the smallest clusters in which the spin-orbit quenching is possible. Evidently, this is due to the restrictions imposed by the spin-orbit relaxation step. The quenching can occur only if the number of solvent molecules in the cluster is sufficiently large, which by itself favors recombination. Additionally, following the electron transfer, the charge in the  $X \cdot I \cdot \cdot \cdot I^-$  state localizes on the escaping fragment, which experiences a backward pull from the solvent. Thus, the solvent configurations that are prerequisite for quenching also favor recombination.

It is noteworthy that if electron transfer fails during the initial fragment separation on the X  $I^- \cdots I^*$  state, the electrostatic force acting on the neutral fragment is weak, and the ensuing dynamics will favor cage escape. Consequently, the dynamical window for spin-orbit quenching is limited to the initial fragment separation, consistent with the fast timescale of caging observed experimentally. Since the quenching step does not add extra time to that needed for fragment separation and subsequent recombination, the similar caging timescales are expected at 395 and 790 nm. This prediction is in accord with the remarkably similar behavior reflected in Fig. 7(a) and (b).

The resonance condition for spin-orbit quenching by solvent asymmetry mediated electron transfer is sensitive to instantaneous solvent configurations.<sup>67</sup> Therefore, the caging reaction involving the spin-orbit relaxation is a sensitive probe of solvation, with the cluster structure playing an important role in the dynamics. In both  $I_2^{-}(OCS)_n$  and  $I_2^{-}(CO_2)_n$  the quenching and caging probabilities are smooth and monotonic outside the range of n = 11-17 (see Fig. 6). Only in the midsize range, where the second half of the first solvent shell is being built, the curves deviate from the monotonic rise. For smaller clusters, the too few available solvent molecules restrict the quenching trajectories because of a limited number of extremely asymmetric solvent configurations that satisfy the requirement  $\Delta \Phi \approx 0.93$  eV. Each additional solvent molecule loosens this constraint, boosting the quenching and caging probabilities. In the mid-size range (n = 11-17), the sufficient degree of differential solvation is achieved without imposing severe dynamical restrictions. In this size range, the details of the cluster structure, not the mere number of solvent

molecules, become crucial in determining the reaction outcomes. This trend continues until the first solvent shell is filled at n = 16-17. From there on, additional solvent molecules do not introduce significant structural changes, and the dynamics revert to a monotonic increase in caging probability with n.

## 4. Structure and photochemistry of homogeneous cluster anions

The properties of cluster anions raise general questions about the reactivity of negative ions in homogeneous and heterogeneous environments. Heterogeneous clusters offer opportunities to study ionic interactions when the charge localization is known and unambiguous. In contrast, homogeneous clusters pose additional questions concerning their structure and the chemical identity of the cluster core. The properties of the core are fundamental to the reactivity and dynamics. The very first question is often whether the excess electron is localized on a single molecule within the cluster or shared between two (or more) monomer moieties.<sup>1,85,109–118</sup> In the limit of electron solvation,,<sup>119,120</sup> the excess electron wave function is delocalized to such extent that the concept of a cluster core is no longer applicable.

In the preceding discussion of solvated  $I_2^{-}$  it was assumed implicitly that during the course of the reaction the charge stays localized on the chromophore or one of its fragments. This assumption is justified, to a degree, in heterogeneous cluster anions, when there is a significant difference in the electron affinities (EA) of the species composing the cluster. Even so, the electronic wave functions of negative ions tend to be defuse, allowing for substantial overlap with the surrounding solvent. For example, even in such a small heterogeneous cluster anion as I<sup>-</sup>·CO<sub>2</sub>, Neumark and co-workers observed a 175° bending of CO<sub>2</sub>, attributed to a small amount of charge transfer from the I<sup>-</sup> to the CO<sub>2</sub>.<sup>121–123</sup> The experiments on hydrated cluster anions by Johnson and co-workers indicate the profound effect that the charge density has on the structure adopted by a water network bound to an ion.<sup>124–129</sup> Charge delocalization can be more important in larger clusters and charge-transfer-to-solvent states are available in both bulk solutions<sup>119,130</sup> and clusters.<sup>131–136</sup>

In the homogeneous water cluster anions  $(H_2O)_n^-$ ,  $n \ge 2$ , the solvent network deforms to trap a diffuse excess electron, forming microscopic precursors of the hydrated electron. Water cluster anions have long served as a favorite system for the studies of electron solvation and the transition between gas-phase and bulk properties.<sup>137</sup> The variety of interactions in these cluster ions, including but not limited to hydrogen bonding and delocalized charge–dipole interactions, lead to interesting structural variations.<sup>76,77,137,138</sup> Significant molecular rearrangements upon electron attachment to a neutral cluster have been implicated in the formation of structural isomers.<sup>137</sup>

Different puzzles pertaining to charge localization and structures are presented by cluster anions of  $\text{CO}_2$ , OCS, and  $\text{CS}_2$ . Since mid-1980s, photofragment and photoelectron spectroscopy, as well as theoretical studies of  $(\text{CO}_2)_n^-$  posed questions of size-dependent alternation between cluster structures adopting either the monomer or dimer anion cores.<sup>110,111,115,139–141</sup> Photoelectron spectroscopy revealed sharp discontinuities in the size-dependence of the vertical detachment energy of  $(\text{CO}_2)_n^-$  between n = 6 and 7 and again between n = 13 and 14.<sup>110,111</sup> These discontinuities have been attributed to "core switching": a transformation of the charged cluster core from a delocalized-charge covalent  $(\text{CO}_2)_2^-$  structure for n < 6 to  $\text{CO}_2^-$  for  $7 \le n \le 13$ , and back to  $(\text{CO}_2)_2^-$  for n > 13. Fleischman and Jordan used electronic-structure calculations to find the global minimum of  $(\text{CO}_2)_2^-$ , which corresponds to a structure of  $D_{2d}$  symmetry with the charge equally divided between the two  $\text{CO}_2$  moieties.<sup>115</sup> The  $(\text{CO}_2)_2^- \rightarrow \text{CO}_2^-$  core switching in  $(\text{CO}_2)_n^-$  at n = 6 was attributed<sup>110,111</sup> to more favorable solvation of the monomer anion, compared to the covalent dimer due to the more localized charge distribution in the latter. The reverse switch occurring between n = 13 and 14 accommodates the dimer-based magic-number structure of  $(\text{CO}_2)_{14}^-$ , *i.e.*  $(\text{CO}_2)_2^- \cdot (\text{CO}_2)_{12}$ .<sup>111</sup>

Photofragmentation studies provide an alternative perspective of the structural properties of cluster anions. Alexander et al. investigated the photofragmentation of  $(CO_2)_n^{-}$  cluster ions<sup>139</sup> and found that they break up exclusively to smaller species of similar composition  $(CO_2)_k^{-}$ , k < n. This behavior may give an impression that no bond breaking or chemical rearrangements are taking place and the fragmentation proceeds merely via the loss of solvent molecules. This is not necessarily the case. The ionic core of these clusters is formed by adding an electron to either the LUMO of a CO<sub>2</sub> monomer or to the combined LUMO of two CO<sub>2</sub> molecules (i.e., a van der Waals dimer).<sup>115,140</sup> Thus, these cluster ions can be viewed as ensembles of closed-shell molecules with an access electron either localized on one of them or shared between two. The only additional covalent bond that may be formed in the cluster anion is the weak (order of 1/2) C–C bond in the (CO<sub>2</sub>)<sub>2</sub> dimer anion.<sup>115</sup> This bond is likely to break after the absorption of a photon, and yet the resulting photofragments are described as  $(CO_2)_k^{-}$ , indistinguishable (in mass) from those formed by solvent evaporation.

Given the isovalency and structural similarity of OCS and  $CO_2$ , one might expect the  $(OCS)_n^-$  cluster anions to be similar to  $(CO_2)_n^-$ . However, the photochemistry of  $(OCS)_n^-$  proved to be a striking deviation from this expectation.<sup>116</sup> The studies of carbonyl sulfide cluster anions began in 1998 with the Lineberger group identifying several types of ionic photofragments of  $(OCS)_n^-$ . In addition to  $(OCS)_k^-$ , which could be expected by analogy with  $(CO_2)_n^-$ , the observed products included  $S_2^-$  and  $S^-/OCS_2^-$  based daughter ions.<sup>116</sup> Such variety of fragmentation channels suggested that extensive bond-breaking and chemical rearrangements take place and attributed to the existence of electronic isomers of  $(OCS)_n^{-.116-118,142}$  In particular, the abundance of  $S_2^-$  based fragments hinted at the role of a covalent dimer anion core with S–S bonding.<sup>116</sup>

Similar discoveries were made for the isovalent  $(CS_2)_n^-$  cluster anions.<sup>86,109,112</sup> Unlike the CO<sub>2</sub> family, where the covalent dimer anion of  $D_{2d}$  symmetry is bound by a relatively weak (order of 1/2) C–C bond, covalent  $(CS_2)_2^-$  and  $(OCS)_2^-$  have most stable structures with planar cyclic geometry of  $C_{2v}$  symmetry. These anions have C–C and S–S covalent bods and are believed to be responsible for the S<sub>2</sub><sup>-</sup> and  $(CS_2)_n^-$  fragments in the photofragmentation of  $(OCS)_n^-$  and  $(CS_2)_n^-$ , respecttively.<sup>109,116</sup> In this light, it may appear intriguing that no cyclic structures were observed in the experiments on  $(CO_2)_n^{-110,111,139}$ 

Jordan and co-workers argued that the  $C_{2v}$  anions of  $(CS_2)_2^-$  and  $(OCS)_2^-$  differ from covalent  $D_{2d}$  symmetry  $(CO_2)_2^{-}$  at a more fundamental level than mere geometry.<sup>116,143</sup> It was suggested that the electronic structure of the  $C_{2\nu}$  species is not derived directly from ground-state CS<sub>2</sub>, OCS, or their respective van der Waals dimers. In the molecular-orbital picture, the removal of the excess electron from the  $D_{2d}$  symmetry  $(CO_2)_2^-$  anion yields two  $CO_2$  molecules in the ground electronic states. To the contrary, the detachment from the  $(CS_2)_2^-$  or  $(OCS)_2^-$  HOMO is predicted to access a neutral electronic configuration which is doubly excited with respect to that of two ground-state CS<sub>2</sub> or OCS molecules, respectively. This configuration arises from a singlet coupling of two CS<sub>2</sub> or OCS molecules excited to the lowest triplet states. Most, but not all, of the combined singlet-triplet excitation energy for two CS<sub>2</sub> or OCS molecules is recovered by the strong bonding in the doubly excited neutral dimer, in which both the strengths of the C-C and S-S bonds are the same as that of a full single bond. Thus, the energetics of the  $(CO_2)_2^-$ ,  $(OCS)_2^-$ , and  $(CS_2)_2^-$  anions are dependent on the singlet-triplet splitting in the respective neutral monomers. In CO<sub>2</sub>, this splitting is significantly larger than in OCS or CS<sub>2</sub>, and as a result, the cyclic dimer anion of CO<sub>2</sub> is less stable.<sup>144</sup>

To fully characterize the electronic and structural isomers one needs to examine their electronic structures. This task is not limited to the discrimination between covalent and electrostatically bound species. Probing the actual orbital structure and relaxation dynamics are of even greater importance. This goal requires new experimental approaches focusing on the electronic structure in the most direct way possible. The next Section describes one such technique that recently emerged as an effective tool for studying cluster structure, reactivity and dynamics.

### 5. Photoelectron imaging of molecular cluster anions

One of the notable recent developments in the field of cluster research is the successful application of photoelectron imaging to molecular cluster anions. The imaging approach to gasphase dynamics was originally developed by Chandler and Houston<sup>78,145</sup> as a tool of photofragment spectroscopy for studying the photodissociation of neutral molecules.<sup>145,146</sup> Several breakthroughs<sup>147–154</sup> led to explosive growth in the field and made the application of imaging to negative ions very compelling. The recent advances in imaging include: velocity mapping, <sup>147,148</sup> event counting, <sup>149,150</sup> and the Basis Set Expansion (BASEX) Abel-transform method.<sup>154</sup> The velocity mapping refined the imaging resolution and made it comparable to that of other spectroscopic techniques. The event-counting approach makes it possible to carry out measurements of very low signals, while the BASEX method has revolutionized the data analysis.

The objectives of imaging studies of photoelectrons (as opposed to photofragments) are best expressed in the context of exploring chemical reactivity at a molecular-orbital (MO) level. Chemistry is often perceived as atomic rearrangements (hence the portrayal of reactions in the generic form  $AB + C \rightarrow A + BC$ ), yet the atomic motions are merely results of more fundamental dynamics involving the transformations of the electronic structure. Chemical bonding is controlled by electrons and it is their behavior that determines the reaction outcomes. Electrons are described by wave functions, *i.e.* the eigenfunctions of the electronic Hamiltonian, yet spectroscopic measurements have traditionally focused on transition frequencies, determined by energy eigenvalues. The challenge pursued by research in the area of photoelectron imaging is shifting the experimental focus on probing the properties of the electronic wave functions themselves (described here in terms of molecular orbitals). The MO transformations are key to reaction dynamics, and thus the objective of these experiments can be seen as unraveling the driving force of chemistry.

Photoelectron imaging visualizes the probability distribution of photoelectrons in the three-dimensional space. Since the x, y, and z coordinates of the photoelectron cloud can be expressed in terms of  $p_x$ ,  $p_y$ , and  $p_z$  (as  $p_x = m_e x/\tau$ , etc., where  $\tau$  is the interval between the detachment event and detection), the experiments measure the projection of  $||\psi_f(\vec{p})|^2$ , where  $\psi_f(\vec{p})$  is the free-electron wave function in the linear momentum space. Due to cylindrical symmetry in experiments with linearly polarized light, the two-dimensional snapshots of photodetachment yield three-dimensional distributions in the laboratory frame, including the speed and angular distributions.<sup>145</sup> The former are converted into photoelectron spectra, while the latter reflect the electronic wave function symmetry<sup>85,155–159</sup> and serve as a portal<sup>105,160–167</sup> for observing the dynamics from the electronic perspective. The application of photoelectron imaging to negative ions<sup>82–87,108,117,118,140,168</sup> demonstrated its applicability to species from atomic anions to molecular cluster anions<sup>86</sup> and indicated several advantages over energy-domain photoelectron spectroscopy.<sup>85</sup> In particular:

(1) The simultaneous observation of the mutually dependent photoelectron angular distributions (PADs) and energy spectra is instrumental for obtaining signatures of the bound orbitals from which the detachment takes place. This feature is of great benefit to the studies of the electronic-structure transformations in several domains important in chemistry, such as: (i) the reaction-coordinate (or time) domain, and (ii) the solvent domain. Time-resolved imaging is used to monitor the evolution of the electronic wavefunction along the reaction coordinate, yielding insights into the reaction dynamics in real time.<sup>108,168</sup> Cluster-size dependent images reflect the changes in the electronic structure due to covalent and van der Waals-type intermolecular interactions implicated in both cluster and bulk environments.

(2) The high sensitivity to slow electrons is an advantage of imaging compared to other techniques of photoelectron detection, such as, for example, the magnetic-bottle time-of-flight method. The feasibility of slow-electron detection extends the routinely observable energy range to zero eKE (electron kinetic energy), enabling the simultaneous observation of both direct and indirect detachment transitions. In several cases, the imaging approach proved key to the assignment of observed transitions.<sup>81–83,86,117,118,140,169</sup>

(3) In the solvent-domain studies of size-selected cluster anions, imaging is impressively effective at revealing the effects of solvation on the competition between different transitions and excited-state decay mechanisms.<sup>117,118</sup>

(4) It has also been shown to be effective in identifying and characterizing the electronic/structural cluster isomers.<sup>85,118,140</sup>

The successful strategy for studying the structure and reactivity of complex clusters using photoelectron imaging involves relying on small molecular anions as reference systems for the interpretation of results for progressively more complex species. Of the  $O_2^-$ ,  $S_2^-$ , and  $CS_2^-$  anions<sup>84–86</sup> employed in the reference capacity,  $CS_2^-$  proved to be a particularly rich model system due to the number of distinct transitions observed and the relevance for comparison with the family of isovalent cluster anions including  $(CS_2)_n^-$ ,  $(OCS)_n^-$ , and  $(CO_2)_n^{-.85,86,117,118,140}$ 

### Small molecular anions

The photoelectron imaging studies of small molecular anions have focused on the general methodology, developing tutorial models for interpreting the results, and establishing a foundation for comparison with more complex cluster-anion systems.

tion for comparison with more complex cluster-anion systems. For example, Fig. 9(a) shows an Abel-inverted<sup>145,154</sup> photoelectron image obtained in  $CS_2^-$  photodetachment at 267 nm.<sup>156</sup> This image is quite remarkable in that it clearly shows three photoelectron bands, each with distinct anisotropy properties, corresponding to electron detachment from three different MOs. Upon closer inspection, a fourth transition can be discerned, corresponding to detachment from one of the above orbitals, but with a different spin. Fig. 9(b) shows a photoelectron spectrum obtained from the image. It is consistent with the previous studies of  $CS_2^{-,84,112,113,170,171}$  however, it is immediately clear that the image contains more structural information than the stand-alone photoelectron spectrum.

The electronic-structure diagram describing  $CS_2^-$  photodetachment is shown in Fig. 10. It includes sketches of the three MOs active in the photodetachment. The bands seen in the image in Fig. 9(a) can be viewed as signatures of these MOs. Interpreting the structure of these bands is important not only out of interest in  $CS_2^-$  electronic structure, but also for understanding how the electrons in these orbitals are affected by



Fig. 9 Photoelectron imaging of  $CS_2^-$ . (a) A 267 nm image showing the transitions to four different electronic states of neutral  $CS_2$ . The laser polarization is vertical. The transitions exhibit different angular distributions and energy bands, characteristic of electron detachment from the specific MOs. The corresponding MOs are indicated as transition labels, with the  $\uparrow$  and  $\downarrow$  subscripts indicating different spin-states of the electron. (b) Photoelectron spectrum obtained from the image in (a).

intermolecular interactions when the anion is solvated in a cluster.

The wave function of the free electron ejected from a bound orbital can be expanded in terms of partial waves with definite values of the orbital angular momentum. For example, detachment from an atomic p orbital yields s and d waves, in accordance with the  $\Delta l = \pm 1$  selection rule. Near the detachment threshold, the cross-section for each wave is approximated by the Wigner law.<sup>172</sup> and thus the relative weight of the isotropic s wave is expected to be greater for slower electrons.<sup>173–175</sup>

Molecular orbitals are generally not eigenfunctions of angular momentum and cannot be assigned specific *l* values. Theoretical treatmentsof angle-resolved ionization of neutral molecules have been under development for over 30 years.<sup>156,157,160–163,176–179</sup> As with experimental work, fewer studies targeted PADs in the photodetachment of molecular anions.<sup>179–181</sup> An important difference between neutral ionization and anion detachment lies in the scaling of partial cross-sections with energy, defined by the different types of long-range interactions of the electron with the positively



Fig. 10 Schematic electronic-structure diagram describing  $CS^{-}_{2}$  photodetachment including sketches of the three active MOs (anion geometry).

charged *versus* neutral core.<sup>174</sup> Many ideas relevant to molecular anion photodetachment have been developed in regards to atomic anions,<sup>175,182</sup> as well as molecular anions with atomic-like MOs.<sup>87,159,183</sup> Other relevant ideas were discussed in the context of threshold photodetachment.<sup>159,174,184,185</sup>

Conceptually, the molecular anion photodetachment can be approached from two distinct viewpoints, discussed in the past in connection with threshold photodetachment.<sup>159</sup> In the first approach, one views the parent MO as a combination of atomic orbitals (AO) located on a single center (not necessarily coinciding with any of the atoms) and then applies the Cooper–Zare central-potential model<sup>156</sup> to each of the MO components to predict the resulting photoelectron anisotropy.<sup>157</sup> This approach works well when the MO expansion in the AO basis includes only a few or preferably just one dominant component.<sup>183</sup> It was used, for example, to interpret the results of S<sub>2</sub><sup>-</sup> photoelectron imaging.<sup>85</sup> Regarding CS<sub>2</sub><sup>-</sup>, the *a*<sub>2</sub> (HOMO – 2) orbital (see Fig. 10) has the same symmetry and basic structure as the  $\pi_g^*$  HOMO of S<sub>2</sub><sup>-</sup>: each of these MOs resembles an atomic d orbital. Not surprisingly, the corresponding detachment bands yield negative values of the anisotropy parameter  $\beta$ ,<sup>145</sup> as characteristic of the p and f partial waves produced in the photodetachment from a d (or d-like) parent orbital.<sup>72,85,181</sup> The pronounced  $\beta < 0$  character of the  $a_2^{-1}$  band in CS<sub>2</sub><sup>-</sup> is clearly seen in Fig. 9(a). The second approach to molecular anion photodetachment

applies to MOs with complex structure which cannot be assigned an effective l value, such as the  $a_1$  HOMO and  $b_2$ (HOMO-1) of  $CS_2^-$  shown in Fig. 10. Also based on the formalism discussed by Reed et al. in the context of threshold photodetachment,<sup>159</sup> this approach relies on group theory to determine the symmetry of the free (photodetached) electron wave function, which is then expanded in a symmetry-adapted single-center AO-like basis. While the scaling of the nearthreshold cross-section is determined by the angular momentum of the lowest-l symmetry-allowed partial wave, 159,174 a more extensive approach is needed for considering the electron ejection anisotropy. Amid the development of rigorous theoretical treatments, there remains a need for qualitative models aiming to provide basic understanding and tutorial description of electron-ejection dynamics without embarking on full-scale quantum calculations. Recently, the Sanov group suggested a model of molecular-anion photodetachment.<sup>84,85</sup> Referred to as the s&p model, this approach builds upon the symmetry-based framework outlined by Reed *et al.*,<sup>159</sup> extending it to the realm of photoelectron angular distributions.

In this model, the orientation averaging inherent in laboratory-frame measurements is accounted for qualitatively by considering only few 'principal' orientations<sup>85</sup> of the anion. Next, the electric-dipole approximation is used in conjunction with the parent MO symmetry to determine the symmetry of the free-electron wave function produced in the detachment from each of the (fixed) principal orientations of the anion. The free-electron waves are then expanded in the basis of s, p, d, f, *etc.* partial waves. The subsequent approximation limits the consideration to s and p partial waves only (hence the model's name), disregarding the contributions with l > 1.<sup>85</sup> This assumption is admittedly crude; however, it is better justified in the case of anion photodetachment than neutral ionization due to the restrictions imposed by the Wigner law.<sup>172–174</sup> The character of the PAD is then determined by considering the allowed s and p waves.

Fig. 11 illustrates the s&p treatment of the (a)  $a_1^{-1}$ , (b)  $b_2^{-1}$ , and (c)  $a_2^{-1}$  photodetachment transition in CS<sub>2</sub><sup>-</sup> assuming a one-electron, MO picture of the detachment.<sup>85</sup> For reference, the photoelectron image bands corresponding to these transitions are indicated by arrows on the left-hand side of the Figure. For each transition, the main panel shows the parent MO in the three principal orientations with respect to the laser polarization axis, followed by the symmetry-allowed s and p



**Fig. 11** The s&p model analysis of the (a)  $a_1^{-1}$ , (b)  $b_2^{-1}$ , and (c)  $a_2^{-1}$  photodetachment channels in CS<sub>2</sub><sup>-</sup>. Left: the (Abel-transformed) photoelectron images with arrows pointing to relevant detachment bands. (Velocity scales are not the same.) The insets in (b) and (c) show an enlarged portion of the 267 nm image containing the partially overlapping  $b_2^{-1}$  and  $a_2^{-1}$  bands, with arrows pointing to the respective bands. Main panels, left: The parent MOs in three principal orientations of the anion with respect to the laser polarization indicated by the vertical arrow at the top. Main panels, right: The symmetry-allowed s and p partial waves contributing to the photodetached wave function.

partial waves contributing to the photodetached electron wave function. In the  $a_1^{-1}$  channel [Fig. 11(a)], three vertically polarized p waves combine with one symmetry-allowed s wave to yield an overall parallel transition ( $\beta > 0$ ). It is also noted that in the vibrationally resolved 800 nm image [the top image in Fig. 11(a)], the anisotropy of photoelectron rings increases with increasing eKE.<sup>84</sup> This trend is predicted by the model, as the relative weight of the p waves should increase with increasing eKE, relative to the anisotropic s wave.<sup>172</sup> In the  $b_2^{-1}$  channel [Fig. 11(b)], two horizontally polarized p waves combine with an isotropic s wave to yield a PAD with a slightly negative  $\beta$ . Finally, in the  $a_2^{-1}$  channel [Fig. 11(c)], no s waves are allowed, resulting in a pronounced perpendicular character of the PAD ( $\beta < 0$ ), as determined by two p waves polarized in the direction perpendicular to the laser polarization.

Despite its simplicity, the s&p model successfully describes not only the general character of photoelectron anisotropy, but also all qualitative trends in  $CS_2^-$  photoelectron images.<sup>85</sup> The model was applied to other molecular as well as cluster anions.<sup>84–86,140,141,186</sup> These applications provide a conceptual foundation for the interpretation of anion photoelectron images, leading to the development of more sophisticated treatments applicable to complex cluster anion systems.<sup>140,141</sup>

### **Cluster anions**

Photoelectron imaging, specifically targeting the electronic structure, is helpful in characterizing molecular cluster anions.<sup>86,117,118</sup> Since the properties of these intriguing species are largely determined by their ionic cores, <sup>1,109,110,113,116,139,187,188</sup> in interpreting the imaging results it is helpful to rely on the data obtained for the unsolvated anions as a starting point providing reference information about the ionic cluster core.

Fig. 12 illustrates the effect of clustering the  $CS_2^-$  anion discussed earlier in this Section with a second CS<sub>2</sub> group.<sup>140</sup> Both raw and Abel-transformed<sup>154</sup> 400 nm photoelectron images are shown for  $CS_2^-$  and  $(CS_2)_2^-$ . While the  $CS_2^-$  image contains a single band (I) with a vertical detachment energy VDE = 1.43eV corresponding to electron ejection from the  $a_1$  HOMO,<sup>84,85,140</sup> (CS<sub>2</sub>)<sub>2</sub><sup>-</sup> yields several transitions. The weak outer band (I) has the energetics (VDE = 1.65 eV) and anisotropy consistent with  $CS_2^-$  solvated by neutral  $CS_2^{,86,140}$ None of the other bands in the image are attributable to the  $CS_2^- CS_2$  structure (since there are not present in the  $CS_2^$ image) and must be ascribed to covalent interaction between the two monomer groups. Thus, the contributions of the coexisting  $CS_2^- \cdot CS_2$  and covalent  $(CS_2)_2^-$  isomers are clearly distinguishable.<sup>86</sup> Band II is assigned to the lowest-energy detachment transition in covalent  $(CS_2)_2^{-1}$ , corresponding to VDE  $\approx 2.7$  eV and  $\beta = -0.17$ . The isotropic spot at the center (III) is mainly due to autodetachment (AD) from the excited state(s) of covalent  $(CS_2)_2^-$  or its photofragments,<sup>86</sup> although some contribution of unresolved direct transitions cannot be



Fig. 12 400 nm photoelectron images of (a)  $CS_2^-$  and (b)  $(CS_2)_2^-$ , shown on the same velocity scale. The raw and Abel-transformed images are shown at the top and bottom, respectively. The laser polarization is vertical. (I) transitions corresponding to electron detachment from the  $CS_2^-$  HOMO (the  $a_1^{-1}$  transition either in the isolated anion or in the  $CS_2^-$ ·CS<sub>2</sub> cluster). (II) lowest-energy detachment transition from covalent ( $CS_2)_2^-$ . (III) Autodetachment from covalent ( $CS_2)_2^$ or its photofragments. Adapted from ref. 140.

excluded. The different properties of the transitions involving the covalent dimer and the  $\rm CS_2^-$  monomer are consistent with the contrasting natures of the corresponding orbitals.  $^{140}$ 

Similar results were obtained for the  $(OCS)_n^-$  family.<sup>117,118</sup> The OCS<sup>-</sup> anion is not formed efficiently in a Lineberger-type<sup>3</sup> electron-impact ion source.<sup>116,189</sup> However, the results for homogeneous  $(OCS)_n^-$  cluster anions can be compared to the OCS<sup>-</sup>·H<sub>2</sub>O cluster anion, providing a way to discriminate between the signatures of the monomer OCS<sup>-</sup> and covalently bound dimer anion cluster cores. In addition, a comparison to  $CS_2^-$  is also useful due to the isovalency of OCS<sup>-</sup> and  $CS_2^-$ .

Fig. 13 displays the photoelectron images of  $CS_2^-$ ,  $OCS^- H_2O$  and  $(OCS)_{2-4}^-$  obtained at a series of photon energies. Besides the different energetics, the  $OCS^- H_2O$  images differ from those for  $CS_2^-$  by the more diffuse nature of the former, as expected for a cluster anion compared to a molecular anion. As a result, the bending vibrational progression<sup>84</sup> seen in the 800 nm  $CS_2^-$  image is absent in  $OCS^- H_2O$ . The otherwise similar features of the  $CS_2^-$  and  $OCS^- H_2O$  images reflect the similarities of the MOs from which the electrons originate.<sup>84</sup>

Unlike the hydrated cluster anions, the homogeneous solvation of carbonyl sulfide anions with additional OCS leads to the formation of electronic/isomers,<sup>116–118,142</sup> in a fashion similar to the  $(CS_2)_n^-$  family.<sup>86,140</sup> The presence of different isomeric species is seen in the  $(OCS)_{2-4}^-$  images in Fig. 13. The higher-eKE parts (I) of these images are similar to their  $OCS^-H_2O$  counterparts, yet the central regions are qualitatively different. The isotropic central spots corresponding to slow electrons in the  $(OCS)_n^-$  images are not present in the  $OCS^-H_2O$  [as well as  $OCS^-(H_2O)_2$ ]<sup>84</sup> results. Overall, the contributions of two different electron-emission mechanisms is evident in the  $(OCS)_n^-$  images in Fig. 13: direct photodetachment (anisotropic bands I, II and III) and delayed autodetachment (AD), while the  $CS_2^-$  and  $OCS^-H_2O$  images reveal only the direct transitions.

These experiments helped round up the general picture of  $(OCS)_n^{-1}$  structure and photochemistry.<sup>118</sup> By virtue of these clusters being an intermediate case between the isovalent  $(CS_2)_n^{-1}$  and  $(CO_2)_n^{-1}$  species, similar conclusions apply to the latter two series. In their interaction with light, the OCSbased clusters exhibit only the direct photodetachment. The dimer-based clusters, on the other hand, are either photodetached directly or promoted to an anionic excited state. The decay of that state, in turn, involves a competition between autodetachment<sup>117,118</sup> and fragmentation.<sup>116</sup> The AD is due to either the excited parent clusters, or internally excited anionic fragments, or an intermediate state. This emission process has been successfully modeled<sup>117,118</sup> as thermionic emission,<sup>81-83,190-193</sup> an effect usually associated with bulk materials. A decrease in the relative autodetachment yield in larger clusters, compared to the covalent dimer, as seen in Fig. 13, is attributed in part to the competition between the AD and fragmentation channels.<sup>118</sup> Thus, both molecular and "bulk" properties are manifest in the excitation of small cluster anions, reflecting not so much the size of these (sub-) objects, but the details of their electronic structure, such as the availability of low-lying excited electronic states.<sup>117</sup>

These results illustrate the utility of photoelectron imaging in the studies of cluster chemistry. The experiments discussed here provide insights into the transformations of the electronic structure in the solvent domain. A natural extension of this approach is probing the evolution of the electronic structure in photoinduced reactions using femtosecond pump–probe photoelectron imaging spectroscopy. This approach has been successfully demonstrated for neutral molecules<sup>79,80,194–196</sup> and for small negative ions.<sup>108,168</sup> Experiments on other molecular and cluster anions are now underway in the Neumark group at Berkeley and the Sanov group at the University of Arizona. As with energy-domain femtosecond photoelectron



Fig. 13 Photoelectron images of CS<sub>2</sub><sup>-</sup>, OCS<sup>-</sup>·H<sub>2</sub>O, and (OCS)<sub>2-4</sub><sup>-</sup> and recorded at 800, 530, 400, and 267 nm. The images are shown on arbitrary velocity and intensity scales (see refs. 84, 85, and 118 for quantitative information). Arrows indicate the contributions of autodetachment (AD) and direct detachment bands I, II, and III. White labels indicate detachment from monomer anion orbitals, yellow-from dimer-anion core species.

spectroscopy,<sup>18,47,133</sup> the femtosecond imaging approach is particularly promising in the cluster field, as it allows examining the transformations of electronic wave functions under the effects of microscopic solvation and in bimolecular encounters.

#### 6. Summary and outlook

This paper reflected on several recent advances in the studies of cluster anion structure and dynamics. We discussed the effects of the solvent on the electronic structure and reactivity of negative ions in homogeneous and heterogeneous solvent environments. Some recent breakthroughs in experimental methodology were outlined, in particular the application of photofragment and photoelectron methods and the imaging technique to the studies of molecular cluster anions.

In the future, we expect an increased emphasis on timeresolved photoelectron spectroscopy and ultrafast coincidence dynamics in the studies of cluster ion reactivity. As more sophisticated experimental tools become available, physical chemists will be able to describe the reaction dynamics in greater detail. The trend towards better-resolved and less-averaged observables is seen in many recent developments, including the growing popularity of the imaging technique (complementary energy and angular distributions), a variety of coincidence methods (correlated product distributions), and time-domain measurements.

Another trend that should not be overlooked by experimentalists is the developments in theoretical chemistry, particularly the explosive growth in computational capabilities. As demonstrated by several examples in this paper, the interpretation of experiments is often dependent on extensive theoretical work. As the theoretical and experimental capabilities reach new levels of elegance and sophistication, chemists acquire the ability to tackle more intriguing questions of structure and dynamics. Many ab initio problems that a decade ago required the computing power of a supercomputer today can be solved at minimal expense using a personal machine in one's office. Thanks to this development, experimentalists can now routinely use the power of computational chemistry to obtain the initial interpretation of results enabling them to navigate more efficiently in search of scientific answers. Such skilful navigation becomes increasingly important, as the sheer dimensionality of information provided by modern state-of-the-art experiments makes their success more dependent than ever on one's ability to ask the right questions.

### Acknowledgements

We thank Prof. Robert Parson and Prof. Kenneth D. Jordan for their collaborations and insights into several projects discussed in this paper. A. Sanov acknowledges the contributions of Dr Richard Mabbs and Eric Surber and support from the National Science Foundation (CAREER Award No. CHE-0134631), the Arnold and Mabel Beckman Foundation (Beckman Young Investigator Award), and the David and Lucile Packard Foundation (Packard Fellowship for Science and Engineering). W. C. Lineberger is pleased to acknowledge support from the National Science Foundation (grants Nos. CHE-0201848 and PHY-0096822) and the Air Force Office of Scientific Research (grant No. F49620-02-1-0371).

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