

# X-ray Induced Coulomb Explosion Imaging of Transient Excited-State Structural Rearrangements in CS<sub>2</sub>

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**Abstract** Structural imaging of transient excited-state species is a key goal of molecular physics, promising to unveil rich information about the dynamics underpinning photochemical transformations. However, separating the electronic and nuclear contributions to the spectroscopic observables is challenging, and typically requires the application of high-level theory. Here, we employ site-selective ionisation via ultrashort soft X-ray pulses and time-resolved Coulomb explosion imaging, to interrogate structural dynamics of the ultraviolet photochemistry of carbon disulfide. This prototypical system exhibits the complex motifs of polyatomic photochemistry, like strong non-adiabatic couplings, vibrational mode couplings, and intersystem crossing. Immediately following photoexcitation, we observe Coulomb explosion signatures of highly bent and stretched excited-state geometries involved in the photodissociation. Aided by a model to interpret such changes, we build a comprehensive picture of the photoinduced nuclear dynamics that follows initial bending and stretching motions, as the reaction proceeds towards photodissociation.

## I. INTRODUCTION

Understanding transient structural rearrangements during photochemical processes is a key step in building a mechanistic picture of chemical and biological pro-

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cesses, such as vision and photosynthesis [1, 2]. Ultrafast lasers, spanning the infrared to the X-ray regime, are critical enabling tools to image the excited-state motion of molecular systems on their natural femtosecond timescales [3, 4]. In recent years the use of diffractive imaging techniques such as ultrafast electron and X-ray diffraction have provided new insights into excited-state structural changes [4, 5]. Alongside these diffractive imaging techniques, Coulomb Explosion Imaging (CEI) with femtosecond laser pulses has emerged as a complementary method to image structural dynamics [6–10]. In notable contrast to diffractive imaging techniques, CEI can exhibit a high sensitivity to light atoms (which have low scattering cross sections), and access high-order structural correlations (i.e., beyond pair distribution functions) [11]. These emerging structural dynamics techniques promise to enable the measurement of ultrafast nuclear dynamics in isolated molecules with high specificity. As such, they offer complementary information to methods such as time-resolved photoelectron spectroscopy and time-resolved X-ray absorption spectroscopy, which are sensitive to both nuclear and electronic dynamics [3, 12]. However, fully disentangling the influence of electronic and nuclear dynamics on these spectroscopic observables is often challenging, and interpretation requires the application of high-level theory [13]. It is hoped that by combining the insights from these different techniques, a more complete picture of the coupled nuclear and electronic dynamics at the heart of molecular photochemistry can be determined.

Coulomb explosion is initiated by the rapid removal of multiple electrons from a parent molecule. The resulting strong internal Coulombic repulsion then causes the multiply charged molecule to explode into ionic fragments. The recorded fragment momenta are correlated to the nuclear geometry of the molecules at the time of multiple ionisation. In many cases, the relative fragment momenta arising from a Coulomb explosion can be understood in terms of simple classical simulations of repelling point charges, whilst in other cases, particularly for lower total charge states, more complex *ab initio* theory may be required [14–16]. Time-resolved Coulomb explosion imaging has found applications in investigating vibrational wavepacket motion [6, 17], dissociation [7, 8, 18] and isomerisation dynamics [19], as well as roaming [10]. Typically, in laboratory-based CEI experiments, intense near-infrared (NIR) pulses are used to initiate Coulomb explosion. Significant strengths of this approach include the ability to approach very high time resolution through use of few-cycle pulses, capitalising on the non-linear nature of the ionisation process itself [20]. However, particularly for longer-duration NIR pulses, nuclear motion within the laser field prior to Coulomb explosion can complicate the interpretation of these experiments. Such motion can be very substantial and may arise due to the sequential nature of strong-field ionisation [7, 21] (prompting dynamics involving intermediate charge states), light-induced coupling of different potentials [22], and the

strong and very non-linear coordinate-dependence of the strong-field ionisation rate (leading to ‘enhanced ionisation’ phenomena) [23]. Consequently, the mapping of initial nuclear structure to final fragment momenta is often complex, and potentially intractable. Multiple ionisation with soft X-ray laser pulses, as produced by Free-Electron Lasers (FELs), may minimise such issues. Photoionisation from a core orbital, followed by Auger-Meitner decay(s), rapidly populates the high charge states required to prompt Coulomb explosion. The negligible ponderomotive potentials of intense X-ray pulses places the light-matter interaction in the multiphoton rather than the strong-field ionisation regime. Furthermore, the ionisation cross-section typically does not (in the absence of resonances) exhibit a highly non-linear nuclear coordinate dependence. As such, short-wavelength FELs are rapidly emerging as very promising light sources for CEI [11, 24].

The target system of the present study, CS<sub>2</sub>, is chosen due to its well-studied and complex non-adiabatic ultraviolet (UV) photodynamics, which are discussed shortly. While the NIR-induced dynamics of CS<sub>2</sub> have been studied extensively [25–27], as have those of isovalent CO<sub>2</sub> [28–30], the present work represents the first application of time-resolved CEI to the UV-induced dynamics of CS<sub>2</sub>. These previous CEI experiments have also demonstrated the significant challenges with traditional intense NIR-based probing. Namely, field-induced couplings of electronic states prompts motion along the bending coordinate, and Coulomb explosion occurs at substantially extended bond-lengths due to enhanced ionisation. By initiating Coulomb explosion through soft X-ray multiphoton ionisation, these deleterious processes are avoided, giving the present work exquisite sensitivity to nuclear structure prior to Coulomb explosion.

Photoexcited CS<sub>2</sub> exhibits many processes of fundamental importance in ultrafast photochemistry, leading ultimately to sub-picosecond photodissociation into both singlet and triplet sulfur atoms, and their correlated CS fragments. Multiple studies have found that production of the spin-forbidden triplet state is dominant, with a branching ratio of approximately 2:1 compared to the spin-allowed singlet sulfur atom [31]. This triplet-dominated branching ratio has recently been ascribed to the rapid formation of a metastable intermediate via internal conversion, which then undergoes intersystem crossing to subsequently produce the triplet sulfur product [32, 33]. Prior to dissociation, excited CS<sub>2</sub> undergoes large amplitude bending and stretching [34–37]. Several values for the mean bend angle that the excited molecule adopts have been reported, ranging from 115° [38] to 153° [39]. Quantum beats have also been observed in the ultrafast studies [32, 35, 40, 41] and attributed to quasi-bound dynamics along the stretch and bend coordinates, prompted by the coherent population of multiple vibronic transitions with sufficiently broadband pump pulses. Differences in observations within the wealth of previous

studies are potentially attributable to the probe pulses used (defined by pulse wavelength, bandwidth and duration), which result in different observation windows in nuclear configuration space, although use of different pump pulses - hence initial wavepacket properties - also play a role. Conversely, spectroscopic (nanosecond) photoproduct studies were able to resonantly probe the distribution of final product states, but did not observe the ultrafast dissociation dynamics directly [42–44]. Significant recent progress has been made through ultrafast photoelectron spectroscopy measurements employing ultrafast vacuum ultraviolet (VUV) probes to allow valence ionisation along the entire reaction coordinate [32, 33]. Here, we extend such ideas further, utilising a soft X-ray probe to study the ultrafast nuclear dynamics through core ionisation, further decoupling the probe process from the (evolving) electronic structure of the photoexcited neutral or final ionised state, giving the present CEI scheme highly specific sensitivity to nuclear dynamics.

Theoretically, the neutral excited-state dynamics have proven particularly difficult to describe accurately since in addition to multiple non-adiabatically coupled singlet states, there is strong coupling to the triplet manifold as well; and all channels involve dissociation. Furthermore, there is a pronounced difference of the wavepacket dynamics on the pump wavelength, as transitions to different vibronic levels of the initially populated  $^1\Sigma_u^+$  state are accessed [31]. The combination of all these factors make for exceedingly difficult first-principles simulations, and previous work has necessitated the use of very high, benchmark-quality *ab initio* computation to achieve even qualitatively correct results [13, 37, 45]. Even in these studies, treating the nonadiabatic and spin-orbit coupling (eg. intra-singlet dynamics and intersystem crossing dynamics) on equal footing was either not attempted [13, 45], or treated using more approximate semi-classical methods [37, 46, 47]. In light of this, one major aim of the present work is to interpret the relationship between the observed time-resolved signals and the nuclear dynamics of photoexcited CS<sub>2</sub> without the input of *ab initio* theory.

In the current work, a 201.5 nm UV pump pulse excites the CS<sub>2</sub> sample prior to multiple ionisation by a 6.9 nm soft X-ray pulse, which initiates Coulomb explosion predominantly through ionisation from the S 2p orbital followed by Auger-Meitner decay(s) [48, 49]. The use of CEI in this experiment allows the excited-state nuclear dynamics of CS<sub>2</sub> to be followed as it proceeds along its reaction coordinate from the predominantly linear ground state geometry, to its bent and stretched excited state, before rapidly decaying to dissociated products. This evolution of the nuclear geometry along non-adiabatically coupled excited electronic states of importance is shown schematically in Fig. 1. Underlying surfaces simulated at the level of theory as described by Wang *et al* [45], are shown to illustrate the driving forces of these photoinduced nuclear dynamics. More detail on the previous calculation of these surfaces is given in the Supplemen-

tary Methods. For simplicity, and to give purely a general overview of the excitation and dissociation process, only relevant singlet states are shown, although we emphasise that triplet states contribute to the final dissociation process [31]. We further emphasise that calculated potential energy surfaces are not used in interpreting the experimental results of the current work, but provide a useful picture of the forces acting on the molecule and the types of structure that can be expected to be sampled as the molecules dissociates. The structural insights extracted from the experiment are enhanced by the use of three-dimensional covariance analysis to extract relative momenta of pairs of ions produced in a given Coulomb explosion process [50, 51]. To further disentangle the large number of soft X-ray-induced fragmentation channels sampled in the experiment, and to relate their appearance to the underlying UV-induced photochemistry, we employ simple Coulomb explosion simulations. These simulations employ a kinetic model of the photodissociation, involving sampling of geometry distributions associated with the ground state and initially populated photoexcited species, which decays to photodissociation products. This approach offers significant insights into the ultrafast nuclear dynamics without the need for challenging, and often infeasible high-level theoretical calculations. Collectively, the current results demonstrate the power of X-ray induced CEI to directly probe the transient structure and ultrafast dynamics of photoexcited species.

## II. RESULTS

Signatures of the UV-induced dynamics of interest are observed in the delay-dependent 3D momentum distributions for a range of ions produced in the experiment. The following discussion focuses on the S<sup>+</sup> and S<sup>2+</sup> ions, which are sufficient to extract a detailed picture of the photoinduced dynamics in CS<sub>2</sub>. A more complete set of delay-dependent momentum distributions of S<sup>(3-4)+</sup>, C<sup>(1-2)+</sup> and CS<sup>(1-2)+</sup>, as well as static and time-resolved mass spectra, are presented in Supplementary Notes 1, 2 and 3.

### A. S<sup>+</sup> Momentum Distributions

Firstly we turn to the delay-dependent momentum distribution of S<sup>+</sup>. As the experiment employs soft X-ray ionisation above the S 2p edge, which is followed by up to two Auger-Meitner decays, S<sup>+</sup> is unlikely to be produced from X-ray ionisation of isolated sulfur atoms [49]. Consequently, S<sup>+</sup> is predominantly produced following multiple ionisation and fragmentation of either bound CS<sub>2</sub> molecules or CS photoproducts, as charge can be effectively redistributed across the molecule, regardless of the initial core ionisation site [52]. Signal arising from Coulomb explosion of excited-state CS<sub>2</sub> molecules

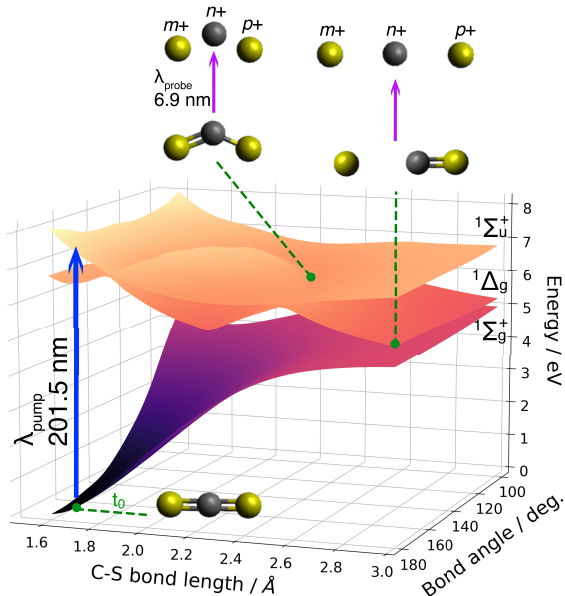


FIG. 1. Title: Schematic representation of the reaction pathway followed by a photoexcited  $\text{CS}_2$  molecule. Legend: Simulated singlet potential energy surfaces for  $\text{CS}_2$ , showing the  $^1\Sigma_g^+$ ,  $^1\Delta_g$  and  $^1\Sigma_u^+$  states [45]. The molecule is excited from the ground state to the optically bright  $^1\Sigma_u^+$  state by the 201.5 nm pump pulse. For the sake of simplicity, photoexcitation is shown to occur from a linear ground state geometry. Example molecular geometries and fragments produced following Coulomb explosion are shown at particular locations along the excited-state potential energy surfaces. Grey denotes carbon, yellow sulfur.

prior to dissociation therefore appears more clearly in the  $\text{S}^+$  ion in contrast to the  $\text{S}^{2+}$  ion, where there is a much greater contribution from ionisation of dissociated S atoms, as is discussed shortly.

Figure 2(a) presents the experimental delay-dependent  $\text{S}^+$  ion momentum distribution. Here, and throughout the manuscript, the differential signal is plotted and obtained by subtracting momenta for pump-probe delays where the FEL precedes the UV by 200-700 fs. The unsubtracted momentum distributions for all ions are provided in Supplementary Note 2. Various depletions occur following photoexcitation due to a reduction in the number of ground-state  $\text{CS}_2$  molecules that interact with the soft X-ray probe. In addition to these depletions, several enhancements stand out in Fig. 2. These include i) enhancement between  $\sim 110$  and 180 a.u. for the first several hundred femtoseconds following photoexcitation, and ii) an enhancement at 90 a.u. and below, which persists to long pump-probe delays. These signals can be related to Coulomb explosions of excited  $\text{CS}_2$  prior to photodissociation, and of CS fragments produced in the photodissociation, as we will show in the following.

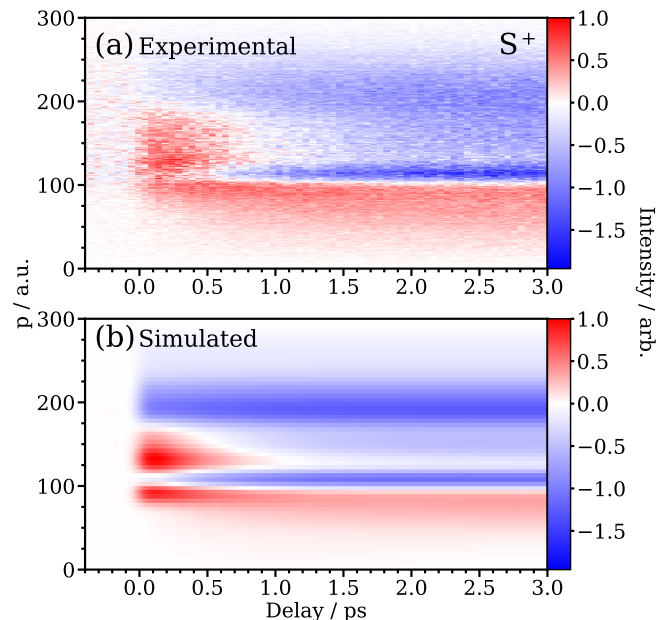


FIG. 2. Title: Delay-dependent difference momentum distribution of the  $\text{S}^+$  ion. Legend: (a) Experimental and (b) simulated delay-dependent difference momentum distribution of the  $\text{S}^+$  ion. Red signal corresponds to enhancements, blue to depletions, relative to pump-probe delays in which the X-ray probe precedes the UV pump. The simulation is produced from summing the nine fragmentation channels that produce an  $\text{S}^+$  ion. A channel-resolved figure showing the individual channels that produce the simulated data is shown in Supplementary Note 7. Momentum is given in atomic units (a.u.).

Experimentally, numerous fragmentation channels are observed, originating from a range of parent charge states produced following interaction with the soft X-ray probe pulse. To aid in the assignment of these features and to unravel their relative contributions, we compare the experimental data with simulations of the photodissociation process and subsequent probing by soft X-ray Coulomb explosion. Despite the simplicity of the modelling, strong qualitative agreement between the experimental and simulated (Fig. 2(b)) delay-dependent momentum distributions is observed by appropriate selection of several parameters, namely: the geometries of the ground-state and excited-state species, the photodissociation timescale and the relative weightings of different photoionisation and fragmentation channels following soft X-ray ionisation.

The modelling process, which relies on a simple physical picture of the predissociation dynamics of  $\text{CS}_2$ , but does not rely on high-level theoretical input, is described in detail in the Methods section, but is outlined here briefly. The photodissociation process was modelled assuming exponential kinetics with a single lifetime, yielding S and CS photoproducts which recoil with a Kinetic Energy Release (KER) sampled from a Gaussian distribution similar to that observed experimentally, and

Coulombic repulsion is simulated at a series of pump-probe delays by placing point charges at the atomic positions and allowing these to repel classically. The simulation includes a geometry change from an approximately linear to bent structure for excited molecules. Whilst a more-complete kinetic model of the UV photodynamics requires multiple time constants, representing dissociation lifetimes of the singlet and triplet dissociation channels [32, 33], here we adopt a simpler scheme given the limited ability for the present experiment to determine a precise delay-dependent singlet and triplet branching ratio (due to their heavily overlapping velocity distributions [42, 43]). The limitations of the singlet-triplet ratio determination are explored in greater detail in Supplementary Note 6.

Differing charge state distributions for ionisation of bound CS<sub>2</sub> and dissociated CS and S were included for each of the ten ionisation channels used in these simulations, to account for differing charge localisation following S 2p ionisation in the bound or dissociated species. Table I lists the observed channels and indicates their relative weightings, which were chosen to optimise the agreement between simulation and experiment. The channels listed in Table I can be interpreted as follows: after dissociation occurs, the two sulfur atoms are no longer equivalent, as one is dissociated (S<sub>a</sub>), whilst the other is bound in the CS fragment (S<sub>b</sub>). Two sets of charge states are given for each channel, corresponding to the charge state distribution at the limiting short and long C-S<sub>a</sub> bond distances, respectively. In the limit of short C-S<sub>a</sub>, the molecule is assumed to be ‘bound’, and charge can redistribute following S 2p ionisation, whilst for extended C-S<sub>a</sub>, charge will remain localised at the fragment containing the ionised sulfur. In Table I and the remainder of the manuscript, three-body fragmenta-

tions are described as  $(m,n,p)$ , which corresponds to the charge of S<sub>a</sub>, C and S<sub>b</sub> ions, respectively. Two-body fragmentations are described as  $(q,w)$ , which corresponds to the charge on S and CS, respectively. To account for structural dynamics prior to dissociation, differing geometry distributions were assumed when simulating the Coulomb explosion of ground-state CS<sub>2</sub> and excited, but undissociated CS<sub>2</sub>.

Analysing the simulated S<sup>+</sup> signal and comparing it to the experimental data in Fig. 2(a) confirms that the ‘transient’ enhancements in the 110-180 a.u. region arise primarily from a reduction of the momentum imparted to the S<sup>+</sup> ion in (1,0,1), (1,1,1), and (2,1,1)/(1,1,2) Coulomb explosions following photoexcitation. This is ascribed to two factors. Firstly, stretching of the C-S bonds in the excited state lowers the total KER of these Coulomb explosion channels. Secondly, excited-state bending of CS<sub>2</sub> results in the partitioning of more momentum from the Coulomb explosion into the C<sup>+</sup> ion (as seen in the time-resolved C<sup>+</sup> momentum distribution shown in Supplementary Note 3), and consequently less into the S<sup>+</sup> ion. This can be intuitively understood by considering the limiting case of a purely Coulombic (1,1,1) explosion of a perfectly linear CS<sub>2</sub>, in which the C<sup>+</sup> would have zero momentum.

Multiple previous studies have reported lifetimes of the excited state, with Farmanara *et al.* reporting a lifetime of 380±20 fs at an excitation wavelength of 200.7 nm, as probed by multiphoton ionisation in the NIR [39]. By contrast, under UV (201.3 nm) pump - UV (~267 nm) probe conditions, a biexponential decay was observed, which included a fast component with ~40 fs lifetime (which was assigned to contributions from hot band transitions from initially vibrationally excited ground-state CS<sub>2</sub>), and a slower component with a lifetime which varied between 510 fs and 640 fs for different relative polarisations of the two pulses [40]. In the recent time-resolved VUV photoelectron spectroscopy study of Suzuki and coworkers, where a broader bandwidth UV pump pulse centred at ~200 nm was used, a <sup>1</sup>B<sub>2</sub> lifetime of 630 fs was reported [32], similar to the 570 fs determined by Minns and coworkers in a similar experimental scheme employing relatively narrow-band pulses [33]. While such lifetimes are in reasonable agreement with the value of 500 fs found here by matching the output of our model to the experimental data, we must stress that the physical meaning of such a lifetime depends on the probe process, the experimental observable and the modelling used to interpret the experimental observations [32, 33]. Similarly, given the existence of multiple vibronic transitions with different lifetimes (e.g., as determined from linewidth measurements, which yield a 500±100 fs lifetime for the transition at 201.2 nm [31]), the spectral content of the pump pulse may significantly affect the observed timescales.

At S<sup>+</sup> momenta of ~100 a.u. and below, enhancements are observed following photoexcitation. The pri-

TABLE I. Title: Coulomb explosion simulation fragmentation channels. Legend: Fragmentation channels specified for the Coulomb explosion simulations. These are specified by charges  $(m,n,p)$  for three-body Coulomb explosions of either S<sub>a</sub>-C-S<sub>b</sub> (bound) or S<sub>a</sub>+CS<sub>b</sub> (dissociated) into S<sub>a</sub><sup>m+</sup>+C<sup>n+</sup>+S<sub>b</sub><sup>p+</sup> and charges  $(q,w)$  for two-body Coulomb explosion into S<sup>q+</sup>+CS<sup>w+</sup>. Channel probabilities were determined by empirical fitting.

| No. | Bound<br>$(q,w)/(m,n,p)$ | Dissociated<br>$(m,n,p)$ | Probability<br>(%) |
|-----|--------------------------|--------------------------|--------------------|
| 1   | (1,1)                    | (2,0,0)                  | 12.5               |
| 2   | (1,1,1)                  | (0,1,2)                  | 17.5               |
| 3   | (2,1,1)                  | (2,1,1)                  | 15.0               |
| 4   | (2,1,2)                  | (2,1,2)                  | 7.5                |
| 5   | (2,0,1)                  | (3,0,0)                  | 10.0               |
| 6   | (1,0,1)                  | (2,0,0)                  | 5.0                |
| 7   | (1,1,0)                  | (0,0,2)                  | 5.0                |
| 8   | (1,1)                    | (0,1,1)                  | 15.0               |
| 9   | (1,0,1)                  | (0,1,1)                  | 7.5                |
| 10  | (1,1,1)                  | (3,0,0)                  | 5.0                |

mary contribution to this is Coulomb explosion of dissociated CS fragments into  $S^+ + C^+$ . The higher momentum signal associated with this process overlaps strongly with depletions of Coulomb explosion channels of bound  $CS_2$ , most notably the (1,1) Coulomb explosion (simulated channels 1 and 8), which results in a depletion at  $\sim 110$  a.u. Once more, this signature of Coulomb explosion of the CS fragment is well reproduced by the simulations, if a sufficiently broad distribution of C-S bond lengths is assumed (1.8 Å mean with 0.4 Å standard deviation), consistent with probing a vibrationally hot CS fragment, as observed previously in nanosecond velocity-map imaging measurements [42, 44].

### B. $S^+$ Covariance Analysis

The assumed bending motion in the excited state can be confirmed by examining the time-dependent angular correlations between the  $S^+$  and  $C^+$  ions. These correlations can be extracted from the data using covariance analysis, as detailed in the Methods section and in previous publications [51, 53]. Due to superior signal-to-noise, we present two-fold covariance analysis, representing the correlations between a pair of ions. Figure S23 in Supplementary Note 11 shows example three-fold covariance analysis, in which delay-dependent signal arising from Coulomb explosion of bent excited-state species can also be resolved. Figure 3 shows experimental and simulated covariances for two different ion pairs, ( $S^+, S^+$ ) and ( $S^+, C^+$ ), plotted as a function of their relative angle and the sums of the magnitudes of their momenta. As in Figure 2, data is plotted as a difference signal, following subtractions of the UV late data. Due to limited statistics, we are unable to extract statistically-robust relative momentum distributions finely resolved over pump-probe delay. Consequently, the two-dimensional covariance histograms for each set of ions are shown integrated over two coarse delay regions defined with respect to the temporal overlap of the two pulses: immediately after overlap ( $< 0.7$  ps), and longer delays ( $> 1.7$  ps). At these delay ranges, the pump-probe signal is dominated by ionisation of photoexcited  $CS_2$  and its dissociated fragments, respectively.

The experimental and simulated covariance images for the ( $S^+, S^+$ ) ion pair are shown in Figs. 3(a)-(b) for delay  $< 0.7$  ps and primarily exhibit contributions from two channels; namely the (1,1,1) and (1,0,1) Coulomb explosion of bound  $CS_2$ . Immediately following photoexcitation, the ( $S^+, S^+$ ) covariance shows transient enhancements at relatively small recoil angles ( $\sim 130^\circ$  for the (1,1,1) channel) (Fig. 3(b)). This provides unambiguous evidence for the (transiently) bent structure of photoexcited  $CS_2$ . As expected, the summed  $S^+$  momentum of  $\sim 230$ -360 a.u. is double that of the transient enhancement observed in the time-resolved  $S^+$  momentum distributions discussed previously. As shown in Figure S7 of the SI, this signal is not observed at long pump-probe

delays, as expected for this transient excited-state feature. We note that the precise summed momentum and relative angle associated with this feature are sensitive to the bond lengths and angles in the excited state. Figures 3(e), (f) show 1-dimensional projections of the difference covariance signal as a function of recoil angle, and summed momentum respectively. These demonstrate the broad agreement between experiment and simulation, observed for a simulated ensemble of excited-state structures with mean C-S length and S-C-S angles of 2.2 Å and  $135^\circ$ , respectively. Similarly, Figure 3(i) presents the integrated covariance signal as a function of pump-probe delay for regions in the two-dimensional covariance histograms corresponding to the transient feature, and from ground state Coulomb explosion. As reproduced by the modelling, a prompt depletion in the ground state signal is observed, as well as a rapid rise and subsequent decay of the transient. In general, the experimental data are more broadly distributed in momentum and recoil angle than the simulation. This is due in part to the finite momentum resolution of the spectrometer, but also due to the simplicity of how the Coulomb explosion is simulated in the model, which neglects deviations from Coulombic forces and assumes instantaneous charging of the molecule. The mean bend angle of  $135^\circ$  reported here is also consistent with the reported degree of early bending in the *ab initio* multiple spawning computational study performed by Wang *et al.* [54]. However, we must caution that the phenomenological geometry distributions used in the modelling to reproduce the experimental signal physically represent a combination of the geometries prior to Coulomb explosion, and the deviations of the ‘true’ Coulomb explosion process from that of our simulation. More detailed theoretical work, particularly in a full simulation of the X-ray induced Coulomb explosion process, will be required to separately discuss these factors.

The covariance analysis for the ( $S^+, C^+$ ) ion pair identifies signal arising from Coulomb explosion of the dissociated CS photoproduct into  $C^+$  and  $S^+$  at longer pump-probe delays. In Fig. 3(c), an enhancement is observed at  $\sim 225$  a.u. total momentum and  $140$ - $180^\circ$ . Figure S7 in Supplementary Note 4 shows the ( $S^+, C^+$ ) covariance for shorter delay values (0-0.7 ps), and again shows the absence of the discussed signal, as most of the events at short delays result from the Coulomb explosion of bound molecules. This can be seen in the delay-resolved covariances shown in Fig. 3(j), where a gradual increase in the signal assigned to CS Coulomb explosion from zero intensity is seen starting from  $\sim 0.2$  ps, consistent with the kinetic modelling. The broad range of momenta associated with this signal implies a wide distribution of bond lengths of the probed CS fragment, consistent with considerable vibrational excitation resulting from the photodissociation [42, 44]. In this case, the covariance analysis cleanly isolates the enhancements from Coulomb explosion of CS from the various depletions of soft X-ray Coulomb explosion channels produced from  $CS_2$  (see

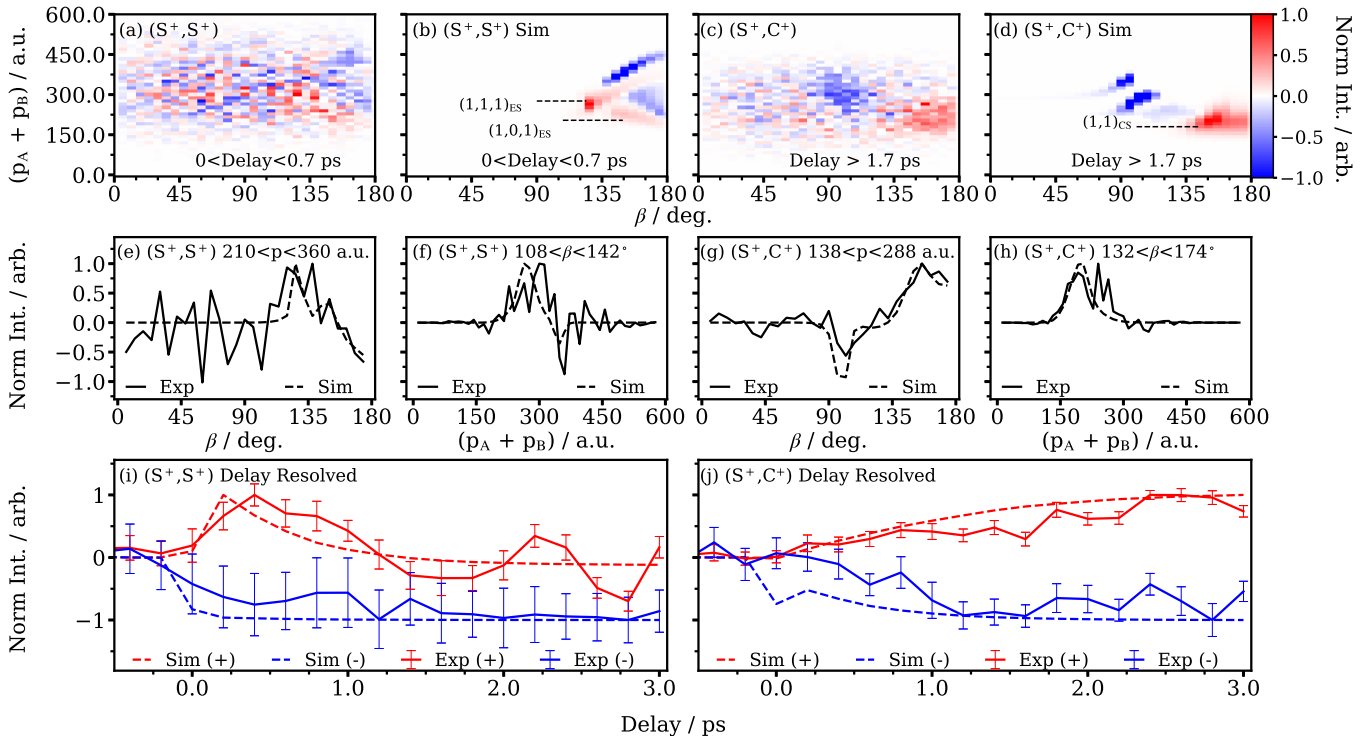


FIG. 3. Title: Delay-dependent three-dimensional covariance analysis. Legend: Three-dimensional covariance analysis for ion pairs  $(S^+, S^+)$  (panels (a) and (b)) and  $(S^+, C^+)$  (panels (c) and (d)) performed for the experimental and simulated data.. Data are presented for different delays between the UV pump and soft X-ray probe to highlight relevant features, as indicated. The covariance signals are plotted as a function of  $\beta$ , the relative recoil angle of the two ions, and the sum of their absolute momenta in atomic units. Highlighted in panels (b) and (d) are excited state enhancements (labelled with subscript ‘ES’). Panels (e) to (h) show 1-dimensional projections with respect to angle and momentum for both the experimental and simulated data of each ion pair. Panels (i) and (j) show 1-dimensional projections of delay as a function of intensity for both the major enhancements and depletions in each experimental and simulated covariance image. Red corresponds to an enhancement and blue corresponds to a depletion. The angle and momentum regions sampled to produce these projections are shown in Fig. S8 in Supplementary Note 4. The time-dependent covariance intensities were normalised to  $\pm 1$  for the enhancements/depletions, respectively, and the error bars were calculated via bootstrapping analysis, where the standard deviation was determined from 200 re-samplings of the data per delay bin.

Supplementary Note 9), representing an advantage over examining the uncorrelated  $S^+$  momentum distribution. This is enabled by the vastly different recoil angles associated with these processes. In the direct X-ray Coulomb explosion of the undissociated molecule,  $C^+$  and  $S^+$  are emitted at roughly  $100^\circ$  from one another, while the Coulomb explosion of CS products yields recoil angles closer to  $180^\circ$ . Typically, for two-body Coulomb explosion, a recoil angle distributed narrowly around  $180^\circ$  is to be expected. However, in this case, the CS fragment acquires significant momentum from the initial photodissociation, broadening the distribution of relative angles following Coulomb explosion, as the initial photodissociation and Coulomb explosion may impart momenta along different directions. Such observations are well reproduced by the simulated data shown in Fig 3(d), once more lending confidence to our assignments. This comparison can be examined in more detail by considering one-dimensional projections of the covariance signal, shown in Figs 3 (g) and (h). The agreement observed supports our

choice of values used for generating the simulations, and hence our subsequent feature assignments using those simulations. We note that some discrepancy between experiment and simulation is seen in the delay-dependent behaviour of the ground-state depletion at early delay times, shown in Figure 3(j). This arises due to overlap between ground-state signal and transient signal related to the electronically-excited species in the experiment, which is more well separated in the simulation, as shown in Figure S7.

### C. $S^{2+}$ Momentum Distributions

Figure 4 shows the experimental (a) and simulated (b)  $S^{2+}$  momentum distributions for the  $S^{2+}$  ion as a function of pump-probe delay.

As mentioned previously, significant qualitative differences between the  $S^+$  and  $S^{2+}$  momentum distributions



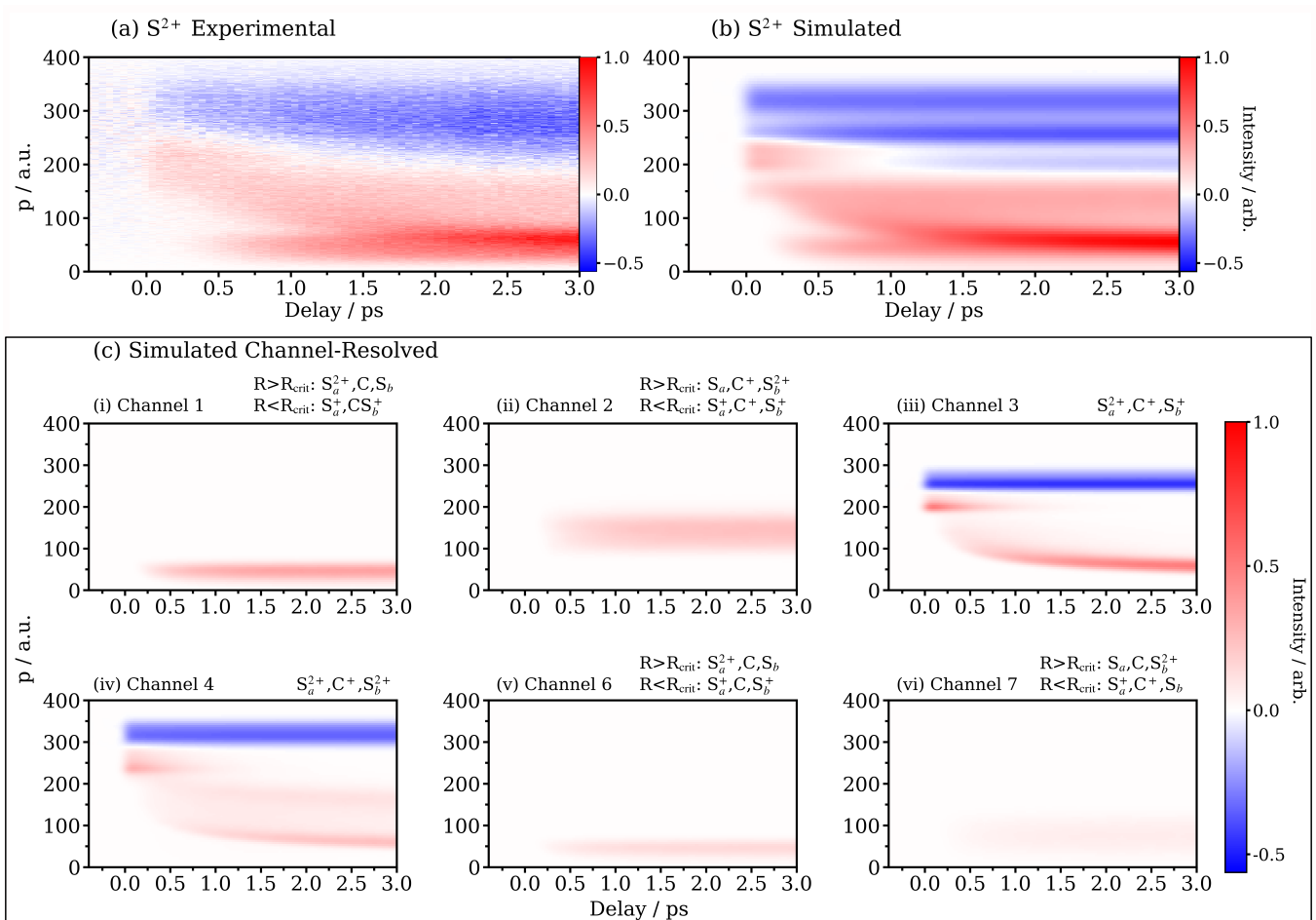


FIG. 4. Title: Experimental and simulated delay-dependent momentum distributions for the S<sup>2+</sup> ion. Legend: Panels (a) and (b) show the full experimental and simulated momentum distributions of S<sup>2+</sup>. Panel (c) shows the main individual fragmentation channels that contribute to the full S<sup>2+</sup> simulation. A detailed discussion of methodology used to generate the simulated difference signal as well as assignment of the channels is provided in the S<sup>2+</sup> Momentum Distributions section. A summary of the relative probabilities of each channel is provided in Table I.  $R_{\text{crit}}$  denotes the separation at which the applied fragment charges changes, corresponding to the localisation of charge at either the S or CS site following soft X-ray ionisation. Values of  $R_{\text{crit}}$  for the different charge transfer processes were calculated using the classical over-the-barrier model and are shown in Table S1 in Supplementary Note 5.

following photodissociation are expected and observed due to the site-selective S 2p ionisation process, which deposits at least two positive charges per photoabsorption [49]. Thus, signal arising from S 2p ionisation of dissociated S atoms may be observed in the S<sup>2+</sup> ion. To more clearly show the contributions from different fragmentation channels, Fig. 4(c) decomposes the simulated delay-dependent S<sup>2+</sup> momentum distributions by fragmentation channel.

Firstly, akin to the transient feature observed in the S<sup>+</sup> momentum distribution (Fig. 2), a transient enhancement is visible within the first picosecond following excitation and between 190-250 a.u. The lifetime and appearance of this channel is attributed to the same origin as the S<sup>+</sup> transient, that is, a transition to a bent and stretched geometry in the excited state. This can be observed in

the simulated fragmentation channels involving Coulomb explosion of bound molecules to a S<sup>2+</sup> ion, namely Channels 3 and 4 in Fig. 4(c). Due to the increased number of fragmentation channels contributing to production of S<sup>2+</sup>, such signal is more heavily overlapped with other enhancements than in S<sup>+</sup>.

Between 80 and 200 a.u., significant variation is observed in the measured momentum across the first few picoseconds, shifting to lower ion momentum at later times. This feature can be linked to a Coulomb explosion of a molecule undergoing photodissociation, as has been noted in several earlier time-resolved CEI studies [6, 8, 9, 18]. At short pump-probe delays (i.e. interatomic distances), we expect additional Coulombic repulsion to contribute significantly to the final ionic momenta when both the S and CS fragments are ionised



by the probe pulse. As the delay between dissociation and ionisation is increased, the Coulombic contribution to the observed total momentum decreases and eventually plateaus, giving rise to the ‘Coulomb curve’ feature. This is clearly observed in Channel 3 (Fig. 4(c)) for the fragmentation channel in which both S and CS photoproducts are doubly ionised. Additional signal at higher momentum ( $\sim 100$ -200 a.u.) persists out to long pump-probe delays, as expected for Coulomb explosion of the CS photoproduct following multiple ionisation into  $S^{2+}$ , as demonstrated in the simulations of Channels 2 and 4 (Fig. 4(c)).

Finally, a low momentum feature is observed between 0 and 80 a.u. with a delayed onset relative to the temporal overlap of the two pulses. This feature can be assigned to double ionisation of dissociated atomic sulfur produced with a neutral CS cofragment, as seen in simulated Channels 1 and 6 (Fig. 4(c)). Analogous features with the same physical origin were also observed in the  $S^{3+}$  and  $S^{4+}$  ion momentum distributions, albeit with differing onset times for each charge state. This variation can be linked to charge transfer after localised photoionisation by XUV or X-ray pulses and can occur for greater internuclear separations for higher charge states. Such behaviour has been observed previously in a range of ultrafast photodissociation studies using site-selective XUV or X-ray probing [55–57]. A discussion of the influence of charge transfer dynamics on this channel is provided in Supplementary Note 5.

As noted in the Introduction, the photodissociation of  $CS_2$  involves dynamics occurring via both the singlet and triplet manifolds [31], which lead to somewhat different velocity distributions of the dissociated photoproducts [42, 43]. Analysis of the corresponding low momentum ( $< 80$  a.u.) feature can provide further insight into the branching between these two channels, owing to different velocity distributions associated with dissociation to either singlet ( $^1D$ ) and triplet ( $^3P$ ) S atom products. A detailed comparison to the nanosecond photodissociation and resonance-enhanced multiphoton ionisation (REMPI) experiments of Brouard and coworkers is provided in Supplementary Note 6 [42, 43]. In line with several previous studies [31, 32], triplet production appears to be favoured, although it should be noted that the expected singlet and triplet velocity distributions heavily overlap, precluding a more detailed channel-resolved analysis.

To conclude, we have presented a time-resolved Coulomb explosion imaging study of UV-excited  $CS_2$ , probed by site-selective multiple ionisation with intense soft X-ray pulses. Aided by covariance imaging analysis and modelling, a picture of the complex photoinduced dynamics was extracted from the recorded delay-dependent ion momentum distributions. This involves rapid motion along stretching and bending coordinates prior to dissociation to  $CS + S$  on longer timescales, consistent with previous spectroscopic measurements. Observed covari-

ant ion momentum distributions arising from Coulomb explosion of the bound excited state, consistent with our modelling for a distribution of geometries with a mean bond angle of  $135^\circ$ , directly confirm the previously assumed bent and stretched excited-state structure. Our study thus represents a key step in the development of CEI as a tool for structural imaging of photoexcited systems, particularly through exploiting the high sensitivity of CEI to bond angles [11, 21, 58, 59], the evolution of which is crucial in the photochemistry of  $CS_2$ . This ability to extract bond angles of photoexcited species remains a challenge for diffractive imaging techniques, which are generally sensitive to the distances between pairs of scatterers [4, 5, 36, 37]. It should be noted that the current experiment was operated at 10 Hz, as limited by the repetition rate of the FLASH pump-probe laser. Ongoing developments in high-repetition rate (kHz-MHz) FELs will allow the full exploitation of multi-dimensional covariance imaging techniques [51, 60–62]. This will extract fully channel-resolved correlated momentum distributions for different Coulomb explosion channels, providing rich structural dynamical information, even for larger molecules. Future work can also exploit recent developments in electron-ion covariance analysis [63] to disentangle the nuclear and electronic contributions to emerging inner-shell photoelectron spectroscopic measurements [13, 63, 64], by extracting spectra associated with a specific Coulomb explosion signature, and thus a group of nuclear structures.

### III. METHODS

#### A. Experimental

Time-resolved CEI measurements on  $CS_2$  were conducted at the CAMP@FLASH instrument [65] on beamline BL1 at the Free-electron LASer in Hamburg (FLASH) [66]. Isolated  $CS_2$  molecules were delivered into the chamber as a continuous supersonic jet, perpendicularly intersecting the pump and probe pulses. A double-sided velocity map imaging (VMI) spectrometer was used to record the three-dimensional momenta of charged ions following multiple ionisation by the FEL. The current work focuses on the ion data collected, while a separate manuscript follows the photodynamics through time-resolved photoelectron spectroscopy [13]. The VMI spectrometer used a detector comprising two stacked micro-channel plates (MCP) in a chevron configuration and a P47 phosphor screen. Electrodes set to velocity mapping potentials directed ions formed in the interaction region along the time-of-flight tube onto this detector. Resulting hits on the P47 screen were recorded using a Timepix3 camera from Amsterdam Scientific Instruments, which was equipped with a  $256 \times 256$  pixel sensor. In addition to the positional information, the camera can also record the pixel time-of-arrival and time-over-threshold with a 1.56 ns and 25 ns precision, respectively

[67]. The temporal and spatial resolution was improved via centroiding, as described for the CAMP setup by Bromberger *et al.* [68]. When coupled with the  $x$  and  $y$  detector position of each ion, this permitted the reconstruction of three-dimensional momenta. Calibration of the fragment momenta was obtained using ion trajectory simulations in SIMION 8.1.

The optical arrangement used in this experiment is similar to Ref. [56], which contains a detailed description of the optical setup. Briefly, the UV pump pulse was generated as the fourth harmonic of a 55 fs, 12 mJ, 800 nm near-infrared (NIR) pulse as follows: two  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO) crystals were used to frequency triple 50% of the NIR beam and dichroic mirrors were then used to isolate the resultant third harmonic. Sum-frequency mixing of the third harmonic with 25% of the original NIR beam (obtained using two successive 50:50 beam splitters) then yielded the fourth harmonic. The resultant UV pulse (201.5±0.4 nm, 0.45  $\mu$ J) was steered into the interaction region by three successive mirrors with a total reflectivity of 48%, giving a pulse energy of 0.22  $\mu$ J at the interaction region. The temporal duration of the 201.5 nm pump pulse was determined via two colour non-resonant multiphoton ionisation of Xe with another NIR pulse within the VMI instrument. A UV/NIR cross-correlation of 150 fs was obtained from this data, which gives a lower limit of the 201.5 nm pulse duration of 140 fs. Taking a previously determined focal spot diameter of 30  $\mu$ m, and accounting for the reflectivity of the mirrors, we estimate a peak UV intensity at the interaction region of  $2.1 \times 10^{11}$  Wcm<sup>-2</sup>.

Intense soft X-ray pulses from FLASH were used to site-selectively ionise and Coulomb explode CS<sub>2</sub> by tuning the photon energy to  $\sim$ 180 eV ( $\sim$ 6.9 nm), above the S 2p edge [48]. Photoionisation of this core orbital predominantly double ionises CS<sub>2</sub>, with a non-negligible contribution from triple ionisation [49]. The FEL operated with an average pulse energy of 54±10  $\mu$ J. Accounting for the losses from transmission along the beamline, this gives an average FEL pulse energy in the interaction region of 23  $\mu$ J. Fluctuations in the FEL pulse energy and timing were tracked on a shot-to-shot basis using the measurements of the Gas Monitor Detector (GMD) [69] and the Bunch Arrival Monitor (BAM) [70], respectively. Based on measurements of the electron bunch charge, photon spectra and the transverse deflecting cavity ‘LOLA’, the soft X-ray pulse duration was inferred to be approximately 90 fs [71]. Assuming a focal spot size of 10  $\mu$ m, this gives a soft X-ray intensity of  $7.2 \times 10^{14}$  Wcm<sup>-2</sup>. The optical laser was overlapped with the soft X-ray probe pulse via a drilled aluminium mirror and recombined in a near collinear geometry. The delay between the UV and soft X-ray pulses was adjusted using a computer controlled delay stage placed in the NIR beampath before the UV generation scheme. Data were recorded at 10 Hz, the repetition rate of the optical and free-electron lasers. The temporal overlap,  $t_0$ , between

the UV and soft X-ray pulses was determined by examining the onset time for production of high momentum C<sup>+</sup> and C<sup>2+</sup>, which yielded a rapid enhancement after UV photoexcitation of CS<sub>2</sub>. Monitoring various ion transient features on a scan-by-scan basis allowed for any temporal drifts not captured by the BAM to be accounted for.

### B. Three-dimensional contingent covariance

By recording the three-dimensional momenta of many ions per FEL shot, correlations between the relative fragment momenta can be determined. In many experiments these correlations are determined through coincidence analysis, which relies on operating at sufficiently low count rates to ensure that on average only a single target molecule is ionised per shot. Under our experimental conditions, an average of  $\sim$ 84 ions were recorded per shot, making such analysis impossible. However, correlated information can still be extracted through covariance analysis [50]. For two ions, A and B, the covariance, a measurement of linear correlation, is calculated as shown in Eq. 1:

$$\text{Cov}(X_A, X_B) = \langle X_A - \langle X_A \rangle \rangle \langle X_B - \langle X_B \rangle \rangle \quad (1)$$

where  $\langle X \rangle$  refers to the mean of the measured quantity  $X$  (ion counts) over a series of observations (laser shots). We exploit a three-dimensional covariance imaging method, outlined in detail in Ref. [51], to extract correlations between ions as a function of their relative three-dimensional momenta. An extension to this methodology, when conducting experiments at self-amplified spontaneous emission (SASE) FELs, is to account for large inherent shot-by-shot fluctuations in the soft X-ray pulse properties [72–75]. We apply a contingent covariance approach (see Ref. [53, 76]) to suppress false contributions to the calculated covariance from correlations produced due to fluctuating FEL pulse energies, which result in all ions appearing correlated. The data is filtered to exclude the low and high power edges of the FEL pulse energy distribution, and then split into specified pulse energy ranges, each containing an equal number of shots. The covariance calculated for each individual energy range is then combined to produce an overall covariance image. This process is expanded upon in Supplementary Note 10.

The high-dimensional data produced from three-dimensional covariance or coincidence ion imaging experiments can be shown in numerous representations (see, for example, Ref. [77]). For the work presented here, we adopt a representation outlined in Ref. [51] where the summed magnitude of a pair of fragment momenta is plotted as a function of relative recoil angle ( $\beta$ ). The signal is binned uniformly in this angle, with no Jacobian correction applied. For a triatomic molecular system such as CS<sub>2</sub>, this has been shown to be an efficient way to track bending during evolving structural dynamics [51, 77].

### C. Coulomb Explosion Imaging Simulations

The individual channels belonging to the momentum distributions of each ion were identified by comparison to Coulombic simulations. These were generated in the following manner. Firstly, for  $10^4$  molecules the photoexcitation process was simulated by assuming prompt population of an excited state, which decayed to a dissociating state with an exponential time constant of 500 fs.

The simulations use representative static distributions of geometries (as explained below) for the ground, excited and dissociated CS<sub>2</sub> states. The CEI results are modelled by manually fitting a set of fragmentation channels and the minimum number of fragmentation channels were utilised to account for all major features. Increasing the quantity of channels would further improve the simulation, but would also greatly increase the difficulty of fitting the probability of each individual channel. For each simulated trajectory, the system is propagated between -500 and 0 fs to provide a background signal and between 0 and 3000 fs to provide a time-dependent signal, and at each time delay Coulomb explosion to model the experimental observables. If a trajectory is yet to be photoexcited, Coulomb explosion occurs from a distribution of geometries representing unpumped molecules. A distribution of bent and stretched geometries is instead used for molecules that are photoexcited but not yet dissociated. The bend angle used for this distribution was determined from the experimental covariance data. The relevant geometry distributions are given in Table II. After dissociation, the S and CS fragments are set to recoil from one another with a constant dissociation velocity. The dissociation velocity was sampled from a Gaussian kinetic energy distribution based upon the experimentally observed distribution of dissociated sulfur atoms. Additionally, available kinetic energy not partitioned into translational energy is assumed to be partitioned into rotation of the CS fragment, which is also accounted for in the dissociation simulation, leading to a rapidly evolving S-C-S bond angle following dissociation. Relevant structural parameters used in the simulations are given in Table II. A mean bend angle of the ground state that is smaller than 180° was used, as is expected for a thermal distribution of a triatomic molecule with a linear equilibrium structure and discussed in detail by Jensen *et al.* for the specific case of CO<sub>2</sub> [78]. The earlier work of Hasegawa *et al* computed an expected mean bend angle of 174° for the vibrational ground level of the electronic ground state of CS<sub>2</sub> [79]. In their NIR-induced CEI study, however, a mean angle of 145° was observed. The better agreement of the mean angle extracted in the present work to the expected value may be due to the use of the soft X-ray probe, which eliminates bending motion prior to Coulomb explosion caused by field-induced couplings of different electronic states [79].

At each time delay in the simulation, Coulomb explosion was modelled by treating ions as Coulombically re-

TABLE II. Title: Structural parameters used in the Coulomb explosion simulations. Legend: Mean and standard deviation of the structural parameters used for the CS<sub>2</sub> Coulomb explosion simulations for ground, excited and bent, and dissociated states.

| Parameter                 | Mean ± Standard Deviation |
|---------------------------|---------------------------|
| Equilibrium C-S length    | 1.55Å±0.1Å [79]           |
| Equilibrium S-C-S angle   | 165.5°±9°                 |
| Excited, bent C-S length  | 2.2Å±0.5Å                 |
| Excited, bent S-C-S angle | 135°±40°                  |
| Dissociated C-S length    | 1.8Å±0.4Å                 |

pellling classical point charges. For the case of a two-body Coulomb explosion of bound CS<sub>2</sub> into CS<sup>+</sup> + S<sup>+</sup>, the point charge in the CS<sup>+</sup> fragment was located on the S<sup>+</sup> atom. For experimentally observed Coulomb explosion channels involving a neutral fragment (e.g., the (1,0,1) and (1,1,0) channels), which cannot be adequately described considering single point charges, a small partial positive charge (uniformly sampled between +0.05 and +0.3) was assigned to the neutral fragment. This assumption yielded qualitative agreement with the experimentally observed data for these channels. This produced sets of differential equations that were numerically integrated, with time steps of 1 fs for the first 400 fs, and subsequent steps of 50 fs out to 5 ps. This outputs a final momentum for each fragment following the Coulomb explosion. For the plotting of simulated delay-dependent momentum distributions, the data were convoluted in pump-probe delay by a Gaussian function of  $\sigma = 50$  fs to emulate the experimental time resolution. Several Coulomb explosion channels were included with ions in initially stationary geometries, and were randomly sampled with different weightings, as listed in Table I. These weightings were determined by empirically by adjusting the weight of each channel to obtain satisfactory agreement with the experimental data. To account for differences in the localisation of charge following S 2p ionisation in bound CS<sub>2</sub> molecules or dissociated S and CS fragments, differing charge state distributions were used in the limit of short and long S-CS bond lengths. In the simulation, this ‘critical distance’, beyond which charge remains localised at the ionised fragment, was set at a bond length of 5.5 Å. A single value of this critical distance was chosen due to simplicity in the modelling. Supplementary Note 5 gives critical distances predicted by a classical over-the-barrier model [55, 80] for a series of possible ionisation and charge transfer pathways. The modelling neglects any contributions from single valence ionisation by the probe pulse, as well as the possibility of producing stable CS<sup>2+</sup> following S 2p ionisation and Auger-Meitner decay. As such, molecular charged CS<sup>n+</sup> fragments are not produced following dissociation and S 2p ionisation in the model. The effects of varying each of the above mentioned simulation parameters are shown in Supplementary Note 8.

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### CODE AVAILABILITY

The codes used to process and analyse the experimental data are available from the corresponding authors on request. The codes to generate the simulated Coulomb explosion are available via an online repository [81].

### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author on request. All steps to reproduce the presented experimental and theoretical findings are either explained in detail or cited in the manuscript.

### AUTHOR CONTRIBUTIONS

The experiment was conceived by R.F., benefited from further input from F.A., B.E. and D.R.. The experiments took place during a remote beamtime at the FLASH facility. The experiment was conducted by H.B., N.E., D.G., E.G., S.K., C.Pap., C.Pas., A.S., A.T.N., J. Mik., A.Röd., A.Rou. and B.E. J.U., F.A., M.Bri., I.G., T.D., D.H., A.J.H., P.H., C-S.L., J.W.L.L., J.M., D.M., W.O.R., T.W. provided online data analysis during the experiment. The experimental data was post-analysed by F.A., M.Bri. and J.U., and the simulations developed by F.A. The interpretation of the data was informed by discussions involving J.U., F.A., I.G., M.Bro., P.H.B., D.M.P.H., R.S.M., M.Schu., A.Sto., C.V., D.R., B.E., M.Bu., R.F. Theoretical support was provided by M.Schu. Manuscript preparation was conducted by F.A., M.Bu., R.F., D.R. and J.U. with input from all authors.

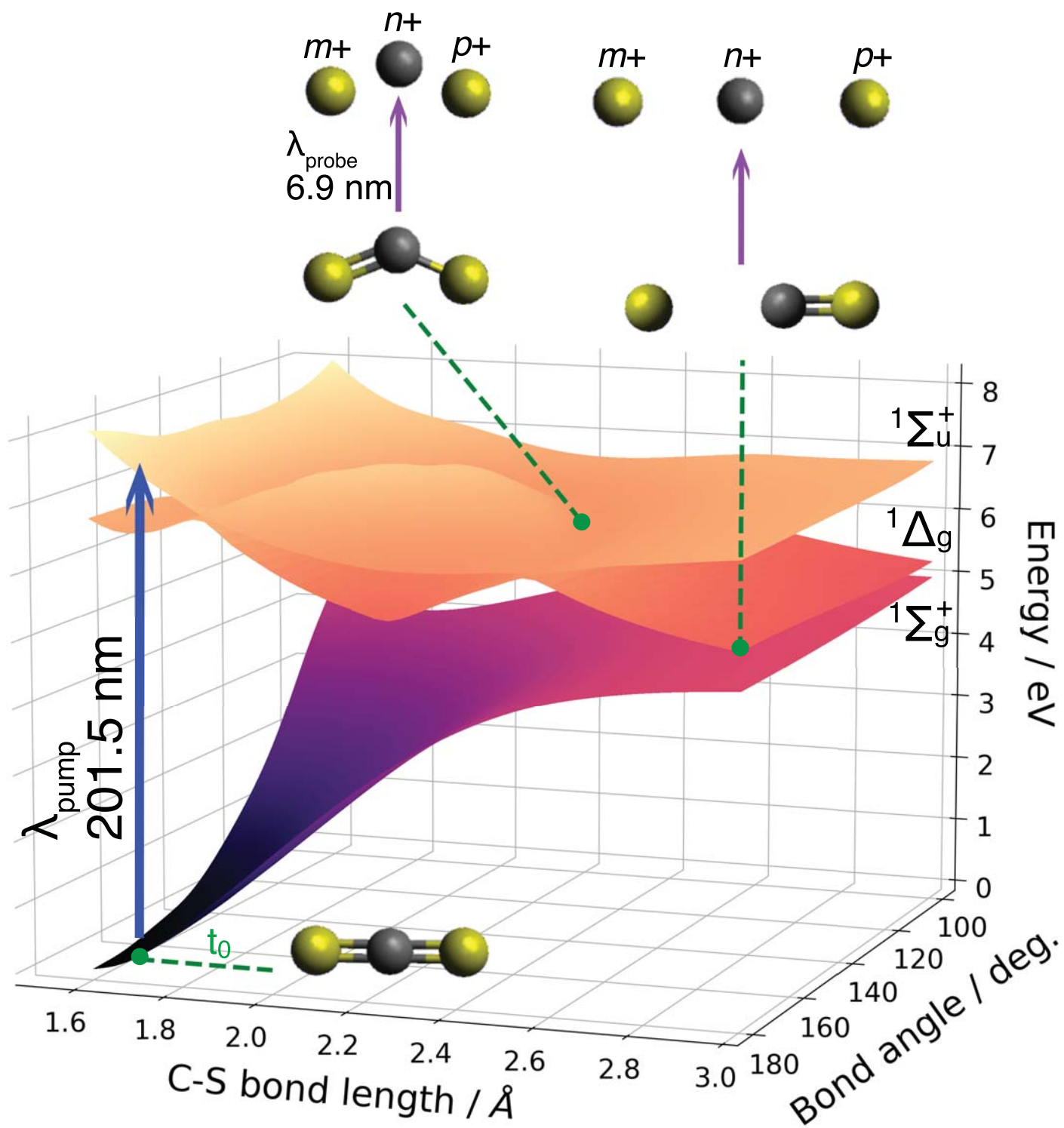
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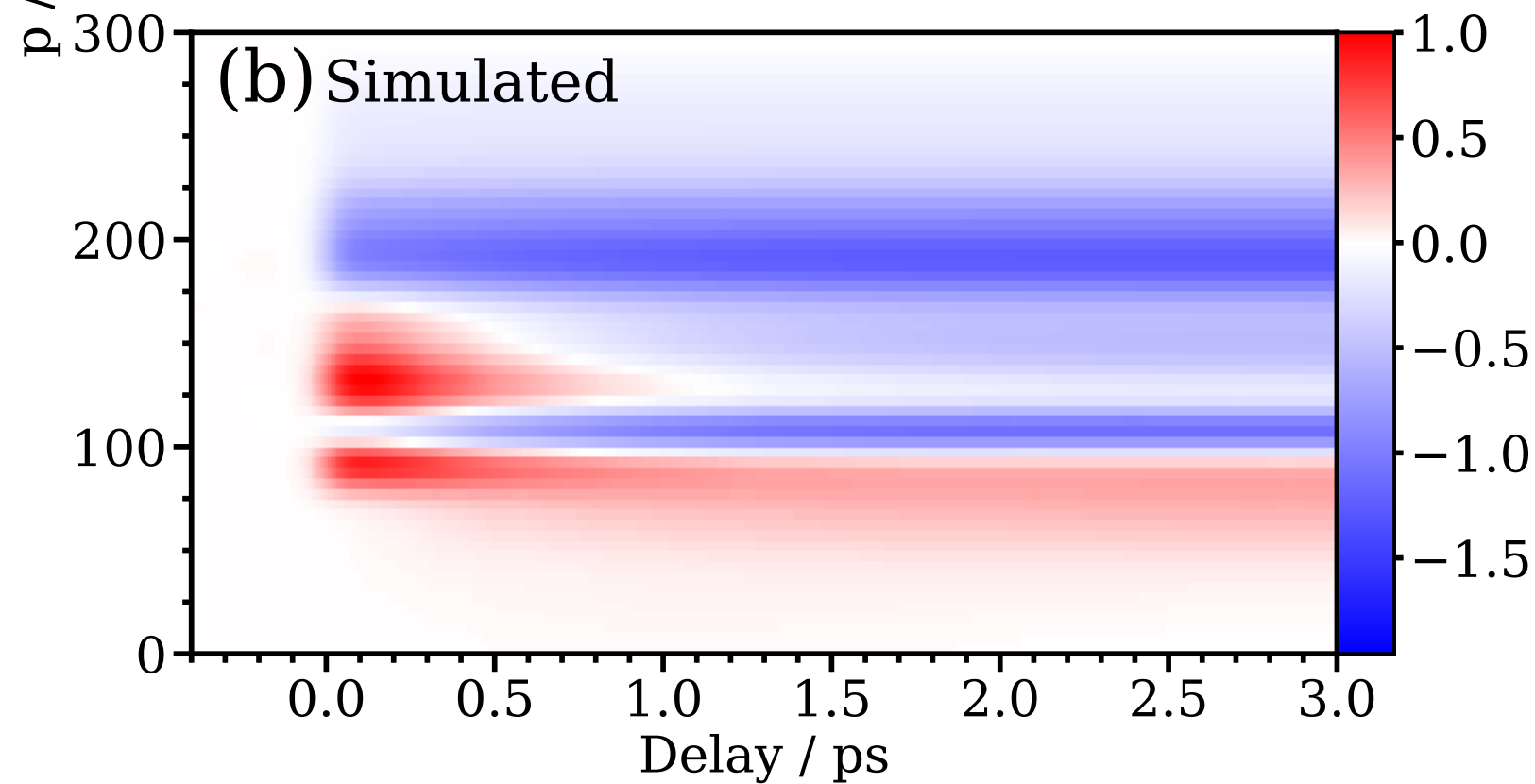
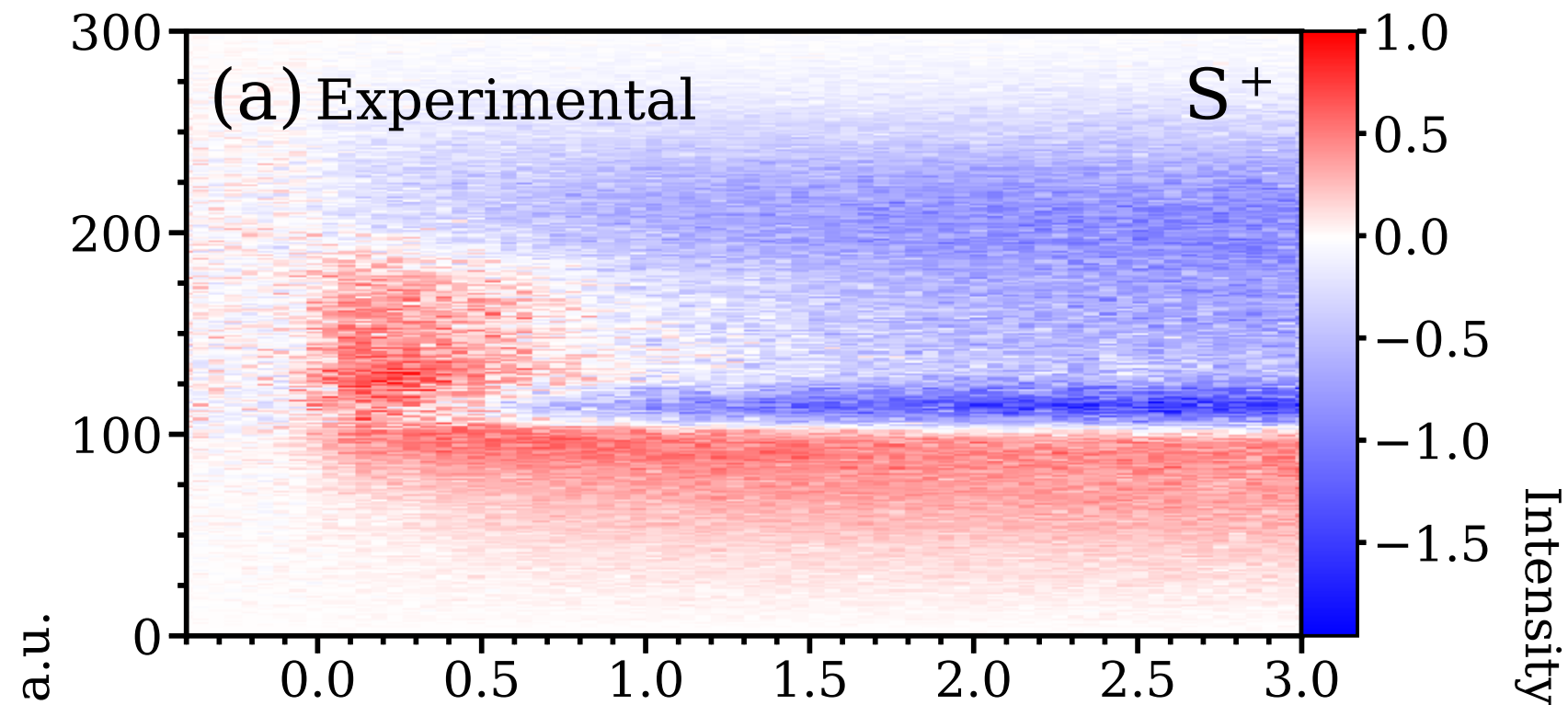
**COMPETING INTERESTS**

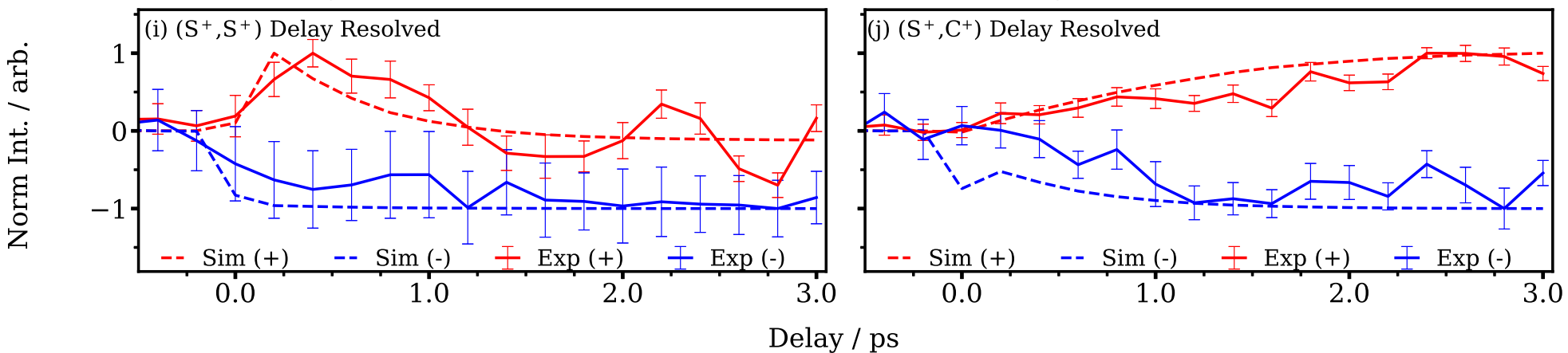
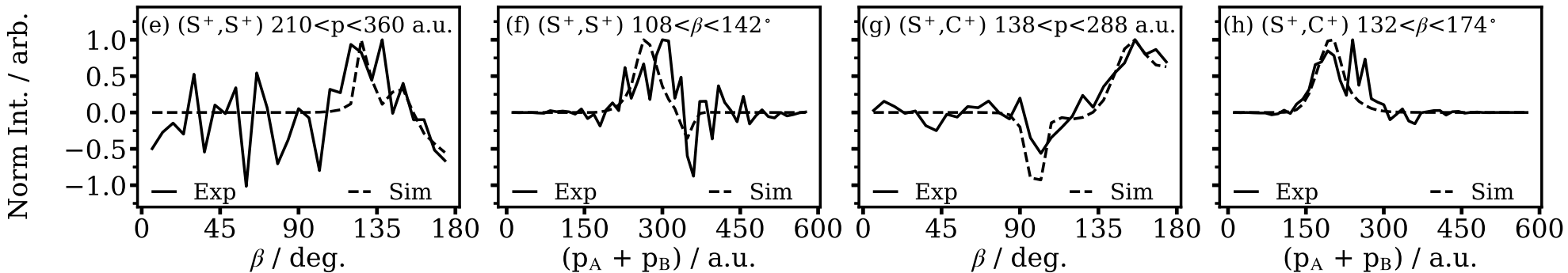
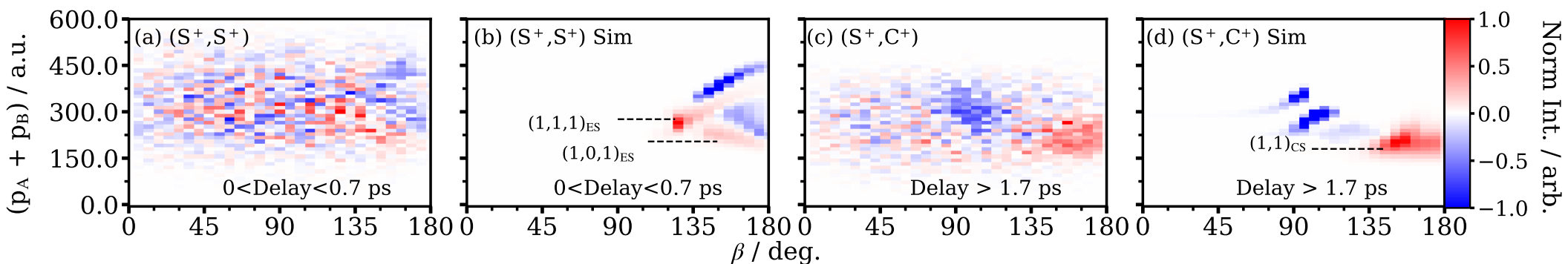
The authors declare no competing interests.

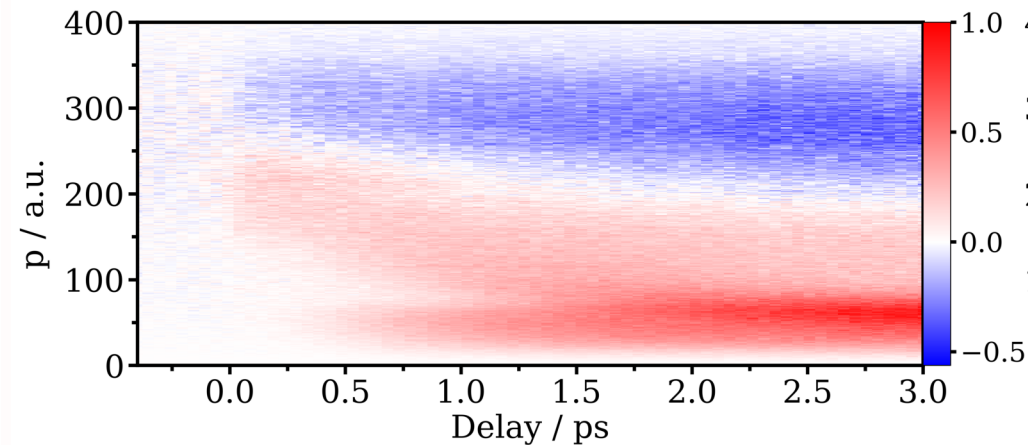
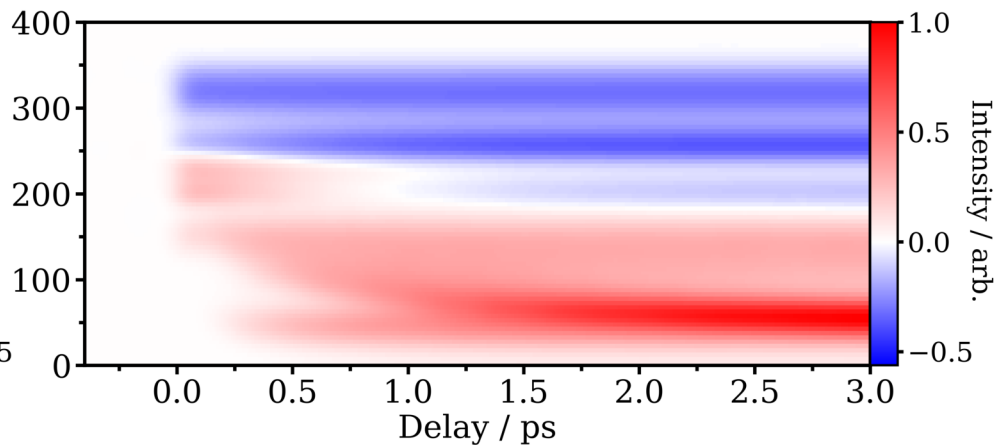










(a)  $S^{2+}$  Experimental(b)  $S^{2+}$  Simulated

(c) Simulated Channel-Resolved

