nature portfolio

Peer Review File

X-ray induced coulomb explosion imaging of transient excited-state structural rearrangements in CS2

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Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The manuscript of Unwin, Allum et al. reports a time-resolved photochemical study of carbon disulfide by means of soft X-ray induced Coulomb explosion imaging (CEI). The experiments are supported by simulation, interpreting the photodynamics of this molecule from the analysis of the delay-dependent momentum distribution of the generated S+ and S2+ ions.

X-ray induced CEI is an emerging, promising, powerful technique to probe nuclear dynamics of photoexcited molecules over time and a challenging playground from both an experimental and computational perspective, with the authors here successfully contributing with new theoretical and experimental insights using a well-known prototypical system.

For these reasons, I believe that the topic and the work of the manuscript could be of interest to the readers of Communication Physics, but major revisions would be needed prior to publication.

M1) The limitation to the analysis of singlet decay channels and the impossibility of obtaining a delay-dependent singlet-triplet branching ratio represent a strong flaw of the work, especially if the goal is to probe the dynamics of a system in which the triplets dynamics is so relevant. While the experimental parts regarding the impossibility of solving the singlet/triplet branching ratio are clear and well-stated, I am wondering if the computational protocol employed, or other calculations, could not be helpful in this direction. A proper scan of singlet and triplet potential energy surfaces involved in the dynamics might be used to obtain more information about dissociative bond distance and angle on the triplet surfaces, as well as to generate a static distribution of geometries. These might be used to simulate trajectories including decay and photodissociation through the triplet channel, for example just starting from a triplet state, if it's not possible to include intersystem crossing in the simulation (which is not clear and should be stated in the methods part).

M2) Nonadiabatic dynamics could be effectively employed to obtain a proper time evolution of the system after light irradiation and the proper geometries to be used to simulate the time-dependent CEI. I am not asking to perform explicit dynamics here, but the authors should at least comment, for completeness, on this and discuss why they preferred the employed approach over it, also referring to previous work on CEI using this approach (J. Phys. Chem. Lett. 2019, 10, 6, 1361–1367 ,https://pubs.acs.org/doi/full/10.1021/acs.jpclett.9b00576).

M3) Figure 1 shows "simulated potential energy surfaces". However, the authors do not give any detail regarding these calculations. Which level of theory is used for the electronic structure calculations? How are the reaction coordinates sampled? This must be stated in the caption to have a meaningful understanding of the figure, and the methodology explicitly reported in the computational details.

M4) More than only the exemplary geometries indicated in Figure 1, the authors could provide optimized geometries at very high level of theory (due to the very limited size of the molecule) at the critical points, indicating calculated bond distances and angles. It would be very important to be able to compare them with the values used and reported in Table II. It would be enough to report them in the supplementary information, but still crucial to obtain a full picture of the study.

M5) Many adjustments of the model seem to be done "ad-hoc" to obtain a qualitatively agreement with the experiment. However, these choices are mentioned but neither really validated nor widely discussed and this makes more speculative the assignment to specific channels. The author should show/comment on what is the effect on the simulation when:
- changing mean and standard deviation of the structural parameters of the distributions
- sampling the channels with different weightings
- including more or fewer channels

- using different charge state distributions
- adjusting the S-CS bond length critical distance

to further validate their assumptions.

M6) How are the trajectories practically simulated? Details about implementation and code use should be given. For example, while it is mentioned how the initial geometries are sampled, it is not said how the simulations account for the different electronic states, i.e. how the trajectories are modeled on different singlet potential energy surfaces.

M7) The authors conclude "Our study thus represents a key step in the development of CEI as a tool for structural imaging of photoexcited systems". However, both experimental and computational limitations and approximation do not seem to really indicate a step towards studying, with this protocol, a more complex and less-known system than the prototypical one used here. I strongly recommend commenting on how the limitations and perspective of this work on using X-ray induce CEI in unveiling the photodynamics of more complex molecules.

Minor points:

m1) The intensity in Figure 3c is assumed from a and b (where the unit is anyway missing) but not specified and it should be added.

m2) Data availability: to ensure the reproducibility of the results, the authors should make the data used in the simulations available upon publication (geometries, fitting parameters, propagator, code).

Reviewer #2 (Remarks to the Author):

I have reviewed the manuscript "X-ray Induced Coulomb Explosion Imaging of Transient Excited-State Structural Rearrangements in CS2" by Unwin et al, submitted to nature communications.
The authors have investigated the excited state dynamics of the prototypical CS2 molecule upon UV photoexcitation and probed by Coulomb explosion imaging induced by free electron laser pulses, imaged by a Timepix camera. Experimental results are accompanied by theoretical simulations.
The results are novel in combining deep UV excitation with soft Xray probing to minimize unwanted coupling effects due to the strong field often used for Coulomb explosion imaging. They aim to provide a clear picture of the resulting nuclear dynamics. Once deeply understood I can see a broad interest in the community for such kind of experiment.
The presented experimental results show the delay dependent S+ fragment momentum distributions with good time resolution which are assigned to excited state dissociation dynamics, averaged over nine fragmentation channels. We see a similar presentation and analysis for the S2+ channel.
To obtain more specific information the authors have performed a covariance analysis between (S+,S+) and (S+, C+) ion pairs. In these cases, the time dependent analysis is reduced to early and late time delays, due to lack of statistics.
The goal of this analysis is to find indications for the bending motion in the excited state and it is compared to simulated data. To see any oscillations in the bending or stretching motion statistics are most probably insufficient so the authors look for characteristic angle distributions. In fig. 3 we find quite noisy and scattered distributions in all the experimental results and structured signatures in the simulated results which are assigned to the different electronic states.
This figure represents the core of the current manuscript and naturally strongly relies on the comparison with theory. My impression is that the authors have looked at their data through the "eyes of a loving mother" when they state a "…strong agreement between the simulations and experiment shown in Fig. 3 …". I can see red and blue blobs in f) that indeed match the position in h) and with goodwill I can also identify some correspondence for the (S+,S+) ion pairs, but I would not call this a strong agreement. This is even worse in the comparison between e) and g).

The authors discuss that deviations between experiment and simulations are due to the fact that experimental data are more broadly distributed in momentum and recoil angle than the simulation and simplicity of the Coulomb explosion.
Certainly, such factors do play a role, and I tend to agree that the overall momentum sum covers similar ranges between both experiment and simulation, as does the angle distribution for long time delays in the (S+,C+) ion pair, but is this already enough to claim a strong agreement? How would the distribution look for other modes of other states, I assume quite similar?
One particular question regarding the simulations: How come the simulations in d) have only negative contributions? In the three other subplots related to simulations we see positive and negative parts but not here. Negative contributions result from subtraction at negative time delays so how is it possible to have only negative parts at pump probe delays >1.7ps?
The authors mention a mean bend angle of 135◦ which I am not able to identify looking at the experimental data. Could they show a projection on the angular axis or any other way to make it visible?
The data discussion for this figure appears rather weak to me. Could the authors try to evaluate their data more by reducing for example angular and/or momentum resolution for a clearer picture to avoid having just scattered red and blue pixel?
Would a separation into more time delays (despite weak statistics) reveal any systematic trend?

The authors discuss the advantage of their approach of using a single photon XUV pulse as the probe pulse compared to commonly used strong field ionization to initiate Coulomb explosion. They especially point out the fact that by initiating Coulomb explosion through soft X-ray multiphoton ionisation, coupling processes that might cause motion along the bending coordinate are avoided, giving the present work exquisite sensitivity to nuclear structure prior to Coulomb explosion. But given the very broad angular distribution they observe in fig.3 I wonder how clear the measured results are. Additionally, already in the abstract it is mentioned that they are employing site-selective ionisation via ultrashort soft X-ray pulses. Nevertheless, I do not see that the authors make use of the site-selectivity in analysing the experimental data, it is only mentioned with regard to the different channels in the simulation. In this context I would like to refer to the following publication: In 2015 Guillemin et al have shown that in the case of CS2 indeed several ionization pathways are possible using similar laser pulses (for the reference see below). I suggest that the authors consider this in interpreting their results.
Furthermore, the authors give the impression that no nuclear dynamics were investigated with strong field ionization. They cite e.g. with ref. 21 the static Coulomb explosion imaging results of Hishikawa et al, omitting that they also investigated nuclear dynamics (see below). Even though these examples do not comprise comparable pump probe experiments they still address nuclear dynamics.

In summary, the authors have investigated the excited state dynamics of CS2 upon excitation with 201nm UV pulses and probed using soft-Xray Coulomb explosion imaging. They presented single fragment analysis as a superposition of different fragmentation channels. They further presented covariance results for ion pairs of the different ion breakups together with a theory analysis. While the results have the potential to address the question of comparability between strong field and multiphoton ionization the current presentation does not look convincing to me. While the simulations suggest a clear picture of the dynamics, it is difficult to see the link to the presented experimental results due to low statistics and the way data is analysed.

Literature:
In general, the authors have cited previous literature appropriately.
However, regarding CS2 and CO2 specific work, relevant references are missing. Especially, but not limited to, the whole body of work of Hishikawa et al is reduced to two examples, not mentioning the work on CS2 nuclear dynamics and CO2 control.
1. Akiyoshi Hishikawa, Hirokazu Hasegawa, Kaoru Yamanouchi, Nuclear dynamics on the light-dressed potential energy surface of CS2 by coincidence momentum imaging, Chemical Physics Letters, Volume 388, Issues 1–3, 2004, Pages 1-6

2. Akiyoshi Hishikawa, Hirokazu Hasegawa, Kaoru Yamanouchi, Sequential three-body Coulomb explosion of CS2 in intense laser fields appearing in momentum correlation map, Chemical Physics Letters, Volume 361, Issues 3–4, 2002, Pages 245-250,
3. Tomoyuki Endo et al, Selective bond breaking of CO2 in phase-locked two-color intense laser fields: laser field intensity dependencePhys. Chem. Chem. Phys., 2017, 19, 3550
4. Xiao Wang et al , Coulomb explosion of CS2 molecule under an intense femtosecond
5. laser field, 2016 Chinese Phys. B 25 053301
6. Guillemin, R., Decleva, P., Stener, M. et al. Selecting core-hole localization or delocalization in CS2 by photofragmentation dynamics. Nat Commun 6, 6166 (2015).

Minor comments:
- Typo in the first paragraph of the introduction: should be sensitive instead of sensitivity
- Typo in the second paragraph of page 5: Supplementary Material
- I suggest to add a reference to table S1 in the caption of fig. 4

We address the comments of the reviewers below where our response is in blue, quotes from MS in green and highlighted changes/additions to MS in red.

Reviewer 1

The manuscript of Unwin, Allum et al. reports a time-resolved photochemical study of carbon disulfide by means of soft X-ray induced Coulomb explosion imaging (CEI). The experiments are supported by simulation, interpreting the photodynamics of this molecule from the analysis of the delay-dependent momentum distribution of the generated S+ and S2+ ions.

X-ray induced CEI is an emerging, promising, powerful technique to probe nuclear dynamics of photoexcited molecules over time and a challenging playground from both an experimental and computational perspective, with the authors here successfully contributing with new theoretical and experimental insights using a well-known prototypical system.

For these reasons, I believe that the topic and the work of the manuscript could be of interest to the readers of Communication Physics, but major revisions would be needed prior to publication.

We thank the referee for noting our successful contributions to the challenging playground of X-ray induced CEI on the prototypical system of CS_2 and for noting the work's interest to the readers of Communication Physics. Outlined below are significant changes to the manuscript addressing each of the raised concerns. We are grateful for the reviewer helping to significantly improve the clarity of the manuscript. As detailed below, we believe several of the raised concerns stem from some misunderstanding about the methodology used in the simulations and the goal of the current work to study ultrafast nuclear dynamics in the absence of high-level theory. In the resubmitted manuscript, we have incorporated several changes to significantly improve the clarity regarding this point.

M1) The limitation to the analysis of singlet decay channels and the impossibility of obtaining a delay-dependent singlet-triplet branching ratio represent a strong flaw of the work, especially if the goal is to probe the dynamics of a system in which the triplets dynamics is so relevant. While the experimental parts regarding the impossibility of solving the singlet/triplet branching ratio are clear and well-stated, I am wondering if the computational protocol employed, or other calculations, could not be helpful in this direction. A proper scan of singlet and triplet potential energy surfaces involved in the dynamics might be used to obtain more information about dissociative bond distance and angle on the triplet surfaces, as well as to generate a static distribution of geometries. These might be used to simulate trajectories including decay and photodissociation through the triplet channel, for example just starting from a triplet state, if it's not possible to include intersystem crossing in the simulation (which is not clear and should be stated in the methods part).

We thank the reviewer for raising this point regarding the role of dynamics on the singlet and triplet manifolds. However, we wish to emphasise that in the current work, the goal is to utilise time-resolved Coulomb explosion imaging to interrogate the *nuclear* dynamics induced following photoexcitation. As is detailed in the second paragraph of the introduction, a powerful capability of X-ray induced Coulomb explosion imaging is the probe's sole sensitivity to nuclear dynamics. As mentioned in the first paragraph of the introduction, spectroscopic observables (e.g., transient absorption spectroscopy, time-resolved photoelectron spectroscopy) are typically jointly sensitive to both electronic and nuclear dynamics, which can complicate their interpretation. As the nuclear dynamics which occur on the singlet and triplet

manifolds are similar (involving bending and stretching prior to dissociation with heavily overlapping product velocity distributions), it is inevitable that a pure structural probe has limited sensitivity to distinguish singlet and triplet pathways. We believe that the purely structural information offered by time-resolved Coulomb explosion imaging has the ability to offer unique and complementary information to traditional spectroscopic probes. This point was previously stated in the final sentence of the first paragraph of the introduction:

"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."

To establish this point more clearly, we have added the following sentence:

"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."

On the role of theory and simulations, this brings us to another key point of the current work, which we apologise for not emphasising clearly enough in the submitted manuscript. Because, to a reasonable approximation, Coulomb explosion signals can often be understood in terms of a classical repulsion between point charges, nuclear structure and thus dynamics can be determined in the *absence of any high-level theoretical calculations*, which are typically technically challenging and, in many cases, currently intractable. We have added the following sentence to the end of the introduction to clearly state this point, and key goal of the current work:

"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"

Throughout the manuscript, several changes in wording have been made to make explicitly clear that the present work is concerned with ultrafast *nuclear* dynamics, and the goal of probing these without employing quantum chemical simulations. This includes the following comment when the simulations are described in the Method section:

"The modelling process, which relies on a simple physical picture of the predissociation dynamics of CS_2, but does not rely on high-level theoretical input, is described in detail in the Methods section, but is outlined here briefly."

M2) Nonadiabatic dynamics could be effectively employed to obtain a proper time evolution of the system after light irradiation and the proper geometries to be used to simulate the time-dependent CEI. I am not asking to perform explicit dynamics here, but the authors should at least comment, for completeness, on this and discuss why they preferred the employed approach over it, also referring to previous work on CEI using this approach (J. Phys. Chem. Lett. 2019, 10, 6, 1361–1367 ,https://pubs.acs.org/doi/full/10.1021/acs.jpclett.9b00576).

We completely agree with the reviewer that nonadiabatic dynamics simulations could be used to simulate time-dependent geometries and thus CEI simulations. As explained above, this approach is not employed in the current work, which instead demonstrates how nuclear dynamics can still be probed without such challenging and time-consuming calculations. We believe that this strength of CEI is key, particularly for systems in which high-level theory is particularly challenging or completely infeasible by current methods. This is often the case for larger molecules and when multiple strongly coupled potential energy surfaces are involved in the dynamics (particularly involving different spin multiplicities and under the presence of strong spin-orbit coupling). As mentioned in response to other comments, we now more explicitly discuss the choice in the current work to describe both the UV-induced and Coulomb explosion dynamics without dynamics calculations. In the introduction, when first discussing Coulomb explosion imaging, we have added mention of the use of classical simulations or higher-level theory, as applied in the paper referenced by the reviewer:

"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."

The neutral excited-state dynamics of CS_2 are particularly challenging to simulate 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 dependence of the wave packet dynamics on the pump wavelength. 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 (Ref 1: *Phys. Rev. Lett.*, 112, 113007, (2014), Ref 2: *J. Chem. Phys.*, 157, 164305, (2022)). 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 (Ref 1), or treated using more approximate semi-classical methods (Ref 2). We believe it is a core-strength of the current approach that results from these time-consuming (and importantly: difficult to benchmark) simulations are not required. This discussion regarding the difficulty of an accurate theoretical description of the photodynamics of CS_2 are now explicitly in a paragraph in the introduction, which comes after discussing previous experimental work on CS_2. This discussion motivates our choice to analyse the present data assuming a kinetic model of the neutral photodynamics.

M3) Figure 1 shows "simulated potential energy surfaces". However, the authors do not give any detail regarding these calculations. Which level of theory is used for the electronic structure calculations? How are the reaction coordinates sampled? This must be stated in the caption to have a meaningful understanding of the figure, and the methodology explicitly reported in the computational details.

We apologise for not including this detail in the submitted manuscript. The simulated potential surfaces shown in Figure 1 were computed using a complete active space self-consistent field (CASSCF) reference function employing a (10,8) active space which then incorporated dynamic correlation at the multi-reference configuration interaction with single excitations (MR-CIS) level of theory and using an atomic natural orbital (ANO) basis: 3s2p1d for C and 4s3p2d for S. These surfaces are the same level of theory as those used in Wang, et. al, *Phys. Rev. Lett.*, 112, 113007, (2014). The reference is now cited in the main body of the text:

“Underlying surfaces simulated at the level of theory as described by Wang et al, are shown to illustrate the driving forces of these photoinduced nuclear dynamics.”

The 2D surface shown in Figure 1 was computed point-wise using a grid of points along the dissociation and angle bend coordinates. However: we emphasise that Figure 1 is meant only to be an illustrative depiction of the relevant potential surfaces and was not employed in the simulations described in this work. For clarity, this is now stated in the text when discussing Figure 1:

“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 above detailed description of the simulated potential energy surfaces has also been added as a section in the Supplementary Information titled “Simulated potential energy surfaces: methods” ‘Theory for PES shown in Figure 1”.

M4) More than only the exemplary geometries indicated in Figure 1, the authors could provide optimized geometries at very high level of theory (due to the very limited size of the molecule) at the critical points, indicating calculated bond distances and angles. It would be very important to be able to compare them with the values used and reported in Table II. It would be enough to report them in the supplementary information, but still crucial to obtain a full picture of the study.

As explained above, the current work applies Coulomb explosion imaging to study nuclear dynamics in photoexcited CS_2 in the absence of high-level theory. As such, we respectfully disagree with the referee that presenting such calculations is necessary. We would also like to emphasise that the ultrafast dynamics of CS_2 cannot be well-explained by specific, highly-optimised geometries. As has been shown by previous theoretical work, a broad distribution of geometries are populated in the excited state, which gradually evolve towards dissociation. Some such work is referred to in the introduction:

“Prior to dissociation, excited CS_2 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° to 153°.”

M5) Many adjustments of the model seem to be done “ad-hoc” to obtain a qualitatively agreement with the experiment. However, these choices are mentioned but neither really validated nor widely discussed and this makes more speculative the assignment to specific channels. The author should show/comment on what is the effect on the simulation when:
- changing mean and standard deviation of the structural parameters of the distributions
- sampling the channels with different weightings
- including more or fewer channels
- using different charge state distributions
- adjusting the S-CS bond length critical distance

to further validate their assumptions.

The choice of ad-hoc adjustments to the various channels giving rise to a given charge states momentum distribution is driven by the overlapping nature of many of the fragmentation channels. If a more rigorous fitting approach was adopted, for more quantitative comparison, the results would be subject to a significant degree of overfitting, hence the current approach allows us to at least qualitatively interpret the

underlying photochemical dynamics. However, we take the reviewers point that understanding the variation in these various parameters is important and to that end an additional section in the Supplementary Information, titled 'Varying Simulation Parameters' has been included. This section contains numerous figures showing the effect of varying each parameter listed above, with differences between the optimised simulation and the experiment discussed.

M6) How are the trajectories practically simulated? Details about implementation and code use should be given. For example, while it is mentioned how the initial geometries are sampled, it is not said how the simulations account for the different electronic states, i.e. how the trajectories are modeled on different singlet potential energy surfaces.

We apologise for the confusion regarding the methodology used to simulate the time-resolved Coulomb explosion signals. The simulations do not employ quantum chemical calculations, there is no concept of potential energy surfaces in the simulation employed. The kinetic model describes prompt excitation to an excited state, which adopts a broad range of (bent and stretched geometries), which exponentially decays to recoiling CS and S photoproducts. The relative velocity distribution of the photoproducts is sampled from a Gaussian distribution, with parameters set to mirror the experimentally-observed photodissociation velocities.

A more detailed description of the simulations in the revised manuscript at the end of the introduction aims to avoid this confusion:

"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."

The following change was made in the Methods section to reiterate this point:

"The modelling process, which relies on a simple physical picture of the predissociation dynamics of CS2, but does not rely on high-level theoretical input, is described in detail in the Methods section, but is outlined here briefly."

M7) The authors conclude "Our study thus represents a key step in the development of CEI as a tool for structural imaging of photoexcited systems". However, both experimental and computational limitations and approximation do not seem to really indicate a step towards studying, with this protocol, a more complex and less-known system than the prototypical one used here. I strongly recommend commenting on how the limitations and perspective of this work on using X-ray induce CEI in unveiling the photodynamics of more complex molecules.

We respectfully disagree with the reviewer that the methodologies presented in our work would not be scalable to the case of unveiling photodynamics in more complex molecular systems. The largest limitation in the present study is the amount of available data to perform the covariance analysis, which is limited due to the 10 Hz repetition rate of the pump-probe laser at the FLASH FEL as well as looking for a relatively small (few percent) change in the experimental signals following UV photoexcitation. This current limitation will be circumvented by the next generation of high repetition rate XFELs (>10 kHz), like LCLS II, which allow data to be collected at several orders of magnitude faster. For scaling to larger systems, another key factor for performing x-ray induced CEI to uncover molecular structures is to extract

the angular covariances for multiple recoiling fragments. This point is showcased via the additional three-fold covariance analysis that we have included in the SI revised manuscript where both delay-dependent correlations between three ions produced in the same process (S^+, C^+, S^+) are shown. Furthermore, members of our collaboration have recently demonstrated the ability to perform four-fold covariance (cumulant) mapping (Reference [57] of the current manuscript), which will enable the structure of significantly larger and more complex molecules to be determined. Static CEI imaging coincidence experiments performed at EuXFEL on iodopyridine (Ref [11]) also support the notion of the correlated measurement of multiple fragments' recoil angles being sufficient to directly image the structure of larger molecular systems.

We revised the conclusions to include some of the above discussion points - "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. On-going developments in high-repetition rate (kHz-MHz) FELs will allow the full exploitation of multi-dimensional covariance imaging techniques [46, 55–57]. This will extract fully channel-resolved correlated momentum distributions for different Coulomb explosion channels, providing rich structural dynamical information, even for larger molecules."

Minor points:

m1) The intensity in Figure 3c is assumed from a and b (where the unit is anyway missing) but not specified and it should be added.

We thank the referee for highlighting this inconsistency. The units have been added to the colorbar in Figure 4b, and an additional colorbar added for Figure 4c.

m2) Data availability: to ensure the reproducibility of the results, the authors should make the data used in the simulations available upon publication (geometries, fitting parameters, propagator, code).

We thank the reviewer for this comment, and we completely agree to sharing this code. Example codes (in the form of a .ipynb Jupyter notebook) will be deposited in an online repository on acceptance of the manuscript. These codes the kinetic modelling of the neutral photodynamics, and the classical simulation of the Coulomb explosion dynamics. Code for plotting time-resolved momentum distributions and relative momentum distributions is also included. The modelling parameters are currently set to those used to produce the distributions shown in the main manuscript, but can be adjusted to reproduce the Supplementary Figures S12-S17 showing the extremes of varying the parameters.

Reviewer 2

I have reviewed the manuscript "X-ray Induced Coulomb Explosion Imaging of Transient Excited-State Structural Rearrangements in CS2" by Unwin et al, submitted to nature communications.
The authors have investigated the excited state dynamics of the prototypical CS2 molecule upon UV photoexcitation and probed by Coulomb explosion imaging induced by free electron laser pulses, imaged by a Timepix camera. Experimental results are accompanied by theoretical simulations.
The results are novel in combining deep UV excitation with soft Xray probing to minimize unwanted coupling effects due to the strong field often used for Coulomb explosion imaging. They aim to provide a

clear picture of the resulting nuclear dynamics. Once deeply understood I can see a broad interest in the community for such kind of experiment.

We are delighted that the reviewer agrees that our results in combining deep UV photoexcitation with soft X-ray induced Coulomb explosion imaging are novel and potentially of broad interest in the community. Detailed below are significant revisions to the manuscript and the inclusion of more-detailed analysis of the time-resolved covariances (resulting in a significantly modified Fig. 3) as well as three-fold covariance results for the (S^+, C^+, S^+) channel to bolster the understanding and significance of the current results.

The presented experimental results show the delay dependent S+ fragment momentum distributions with good time resolution which are assigned to excited state dissociation dynamics, averaged over nine fragmentation channels. We see a similar presentation and analysis for the S2+ channel.
To obtain more specific information the authors have performed a covariance analysis between (S+,S+) and (S+, C+) ion pairs. In these cases, the time dependent analysis is reduced to early and late time delays, due to lack of statistics.
The goal of this analysis is to find indications for the bending motion in the excited state and it is compared to simulated data. To see any oscillations in the bending or stretching motion statistics are most probably insufficient so the authors look for characteristic angle distributions. In fig. 3 we find quite noisy and scattered distributions in all the experimental results and structured signatures in the simulated results which are assigned to the different electronic states.
This figure represents the core of the current manuscript and naturally strongly relies on the comparison with theory. My impression is that the authors have looked at their data through the “eyes of a loving mother” when they state a “…strong agreement between the simulations and experiment shown in Fig. 3 …”. I can see red and blue blobs in f) that indeed match the position in h) and with goodwill I can also identify some correspondence for the (S+,S+) ion pairs, but I would not call this a strong agreement. This is even worse in the comparison between e) and g).
The authors discuss that deviations between experiment and simulations are due to the fact that experimental data are more broadly distributed in momentum and recoil angle than the simulation and simplicity of the Coulomb explosion.
Certainly, such factors do play a role, and I tend to agree that the overall momentum sum covers similar ranges between both experiment and simulation, as does the angle distribution for long time delays in the (S+,C+) ion pair, but is this already enough to claim a strong agreement? How would the distribution look for other modes of other states, I assume quite similar?

We agree with the reviewer’s comment that to those unfamiliar with the data the agreement between experimental and simulation is difficult to see. To aid in this we have updated Figure 3 to include 1-dimensional line-outs of angle, momentum and delay with respect to intensity that shows broad agreement between the onset and rise times of the discussed experimental and simulated features. The covariance images that do not show the enhancements that are discussed in detail in the main text have been moved to Figure S7 in the Supplementary Information.

One particular question regarding the simulations: How come the simulations in d) have only negative contributions? In the three other subplots related to simulations we see positive and negative parts but not here. Negative contributions result from subtraction at negative time delays so how is it possible to have only negative parts at pump probe delays >1.7ps?

We are happy to provide clarification on the above comment. The lack of positive signal is due to the dominant channels occurring at this delay range being the Coulomb explosion of the dissociated CS fragment, which generally leads to a singly charged sulfur ion as well as a charged carbon ion. When ionising the neutral S atom, above the S 2p edge, multiply charged S^{n+} ions are almost exclusively produced hence there should not be any positive contributions to the (S^+,S^+) covariances at long delays, once the dissociation is complete. This situation is, however, very different to early time dynamics where two singly charged sulfurs can be produced from the Coulomb of bound and photoexcited CS_2.

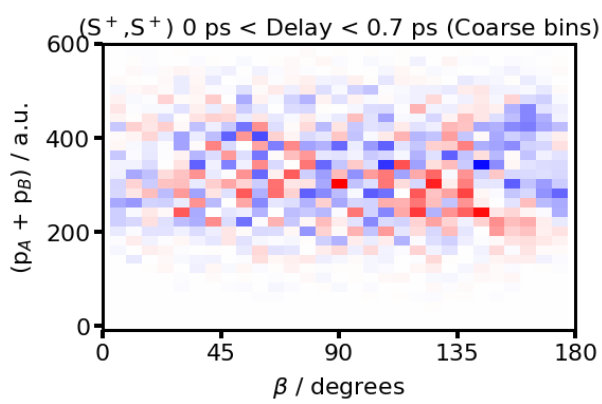
The delay resolved plots now included in Figure 3(i) and (j) support this assignment, with the (S^+,S^+) covariance intensity peaking shortly after t0 and decaying down to zero intensity at later delays, while the (S^+,C^+) covariance starts at zero intensity and increases to a maximum at late delays.

The authors mention a mean bend angle of 135◦ which I am not able to identify looking at the experimental data. Could they show a projection on the angular axis or any other way to make it visible?

We thank the reviewer for their suggestion of including 1D projections of the covariance data. As mentioned above Figure 3 has been updated to include both angular and momentum cuts of the theoretical model and experiment data for the (S^+,S^+) and (S^+,C^+) channels. We would like to make it clear that the recoil angle between the two sulfurs is not the same as the bond angle prior to excitation, although the two are closely related.

The data discussion for this figure appears rather weak to me. Could the authors try to evaluate their data more by reducing for example angular and/or momentum resolution for a clearer picture to avoid having just scattered red and blue pixel?

We thank the reviewer for their suggestion of decreasing the momentum resolution to enhance the signal. However, as shown below, increasing the (S^+,S^+) covariance momentum bin size increased from 12 a.u. to 20 a.u. provides minimal enhancement in signal quality. We hope that the inclusion of the above discussed 1-dimensional lineouts to Figure 3 are suitable for resolving any concerns about the agreement between the experimental and simulated covariance data.



Would a separation into more time delays (despite weak statistics) reveal any systematic trend?

We are grateful to the reviewer for suggesting this and have performed some time-resolved analysis of the (S^+,S^+) and (C^+,S^+) covariances. The experimental regions in angle and momentum, showcased in Figure S8, were integrated over and the associated temporal dynamics was investigated over a range of a few picoseconds in 200 fs steps. The outcome of this analysis is showcased in Figure 3 panels (i)-(j) and highlights the similar onset times and intensities of both the signal increases and depletions between the experimental and simulated covariance images.

The text in the section 'S^+ Covariance Analysis' in the main manuscript has been reworked to include discussion of both these time resolved features as well as the angular and momentum line-outs described above.

The authors discuss the advantage of their approach of using a single photon XUV pulse as the probe pulse compared to commonly used strong field ionization to initiate Coulomb explosion. They especially point out the fact that by initiating Coulomb explosion through soft X-ray multiphoton ionisation, coupling processes that might cause motion along the bending coordinate are avoided, giving the present work exquisite sensitivity to nuclear structure prior to Coulomb explosion. But given the very broad angular distribution they observe in fig.3 I wonder how clear the measured results are.

The ability of soft x-ray ionisation to more faithfully recover the geometry at the point of ionisation can be seen through the comparison of our ground state (static) Coulomb explosion data with the previous literature from Hishikawa and Yamanouchi exploring the near-infrared Coulomb explosion of CS_2. As discussed in the Methods subsection "Coulomb explosion imaging simulations" - "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 CS2 [24]. 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 is due to the use of the soft X-ray probe, which eliminates bending motion prior to Coulomb explosion induced by field-induced couplings of different electronic states [24]." In the present work we recover a mean bond angle of 165.5 degrees, which is significantly closer to the 174 degrees expected from this earlier theoretical work.

To date no experiments have been conducted exploring the ability of intense near-infrared Coulomb explosion imaging to track the UV induced excited state dynamics of CS_2, so this direct comparison, although very interesting, is currently beyond the scope of the present work.

Additionally, already in the abstract it is mentioned that they are employing site-selective ionisation via ultrashort soft X-ray pulses. Nevertheless, I do not see that the authors make use of the site-selectivity in analysing the experimental data, it is only mentioned with regard to the different channels in the simulation. In this context I would like to refer to the following publication: In 2015 Guillemin et al have shown that in the case of CS2 indeed several ionization pathways are possible using similar laser pulses (for the reference see below). I suggest that the authors consider this in interpreting their results.

For the case of Coulomb explosion of intact molecules, the site-selective nature of the probe is of comparatively little importance, because while the initial ionisation even is predominantly from the S 2p orbital, following Auger-Meitner decay the charge is well redistributed about the entire molecule, leading to a wide range of possible Coulomb explosion channels. We are thankful to the referee for suggesting the inclusion of the 2015 paper of Guillemin *et al* in our references. This has been added as part of the following change to the manuscript:

“Consequently, S^+ is predominantly produced following multiple ionisation and fragmentation of either bound CS_2 molecules or CS photoproducts, as charge can be effectively redistributed across the molecule, regardless of the initial core ionisation site.”

However, we note the ionising radiation used in the present work and this study is rather different. Here we exploit multiphoton ionisation above the S 2p edge (~180 eV) at a XFEL whereas the single-photon coincidence work of Guillemin and coworkers was conducted at synchrotron SOLEIL at a photon energy of 2488 eV, which lays above the S 1s edge.

With regards to the nature of site-selective probing in our current experiment we have softened some of our wording here but note that this does play a role in the presented data. For example the S^+ ion exhibits sensitivity to the bound species (photoexcited neutral CS_2, the dissociated CS photoproduct, etc.) whereas S^{2+} preferentially samples the dynamics associated with the dissociated S atom, due to photoionization and subsequent Auger-Meitner process leaving the system with at least two charges when ionising above the S 2p edge. We note that this mapping of the photoinduced dynamics is likely to be very different for the cases for example inner ionisation at C K-edge as well as strong-field based methods.

We have clarified the role of the site-selective nature of probe in a number of places in the manuscript, e.g.:

“As mentioned previously, significant qualitative differences between the S^+ and S^{2+} momentum distributions following photodissociation are expected and observed due to the site-selective S 2p ionisation process, which deposits at least two positive charges per photoabsorption.”

Furthermore, the authors give the impression that no nuclear dynamics were investigated with strong field ionization. They cite e.g. with ref. 21 the static Coulomb explosion imaging results of Hishikawa et al, omitting that they also investigated nuclear dynamics (see below). Even though these examples do not comprise comparable pump probe experiments they still address nuclear dynamics.

We are thankful to the reviewer for catching this error and certainly did not mean to omit this important literature from the discussion in our study. The references provided below have been added to the introduction of the manuscript to highlight these points.

As noted by the reviewer a key novelty of this manuscript is investigating the deep UV induced dynamics in CS_2 unlike many previous studies that have focused on strong-field ionisation. It is therefore difficult to directly compare any of the current pump-probe results to this previous literature. Additional text in the introduction specifically refers to the earlier strong-field work, as well as the lack of previous UV pump time-resolved CEI experiments on CS_2:

“While the NIR-induced dynamics of CS_2 have been studied extensively, as have those of isovalent CO_2, the present work represents the first application of time-resolved CEI to the UV-induced dynamics of CS_2.”

In summary, the authors have investigated the excited state dynamics of CS2 upon excitation with 201nm UV pulses and probed using soft-Xray Coulomb explosion imaging. They presented single fragment analysis as a superposition of different fragmentation channels. They further presented covariance results for ion pairs of the different ion breakups together with a theory analysis. While the results have the

potential to address the question of comparability between strong field and multiphoton ionization the current presentation does not look convincing to me. While the simulations suggest a clear picture of the dynamics, it is difficult to see the link to the presented experimental results due to low statistics and the way data is analysed.

We are grateful to the reviewer for highlighting the comparison of strong-field/multiphoton ionisation based Coulomb explosion imaging with the current soft x-ray based work. As outlined above we did provide some discussion of the comparison of the static ground state Coulomb explosion data with the previous literature of Yamanouchi and coworkers but the direct comparison for the case of UV excited CS_2 is not possible as these experiments have not to our knowledge been performed. However, although this investigation is beyond the scope of the current work it remains a very interesting question/comparison and could form the basis for follow up work and future studies.

Literature:
In general, the authors have cited previous literature appropriately.
However, regarding CS2 and CO2 specific work, relevant references are missing. Especially, but not limited to, the whole body of work of Hishikawa et al is reduced to two examples, not mentioning the work on CS2 nuclear dynamics and CO2 control.
1. Akiyoshi Hishikawa, Hirokazu Hasegawa, Kaoru Yamanouchi, Nuclear dynamics on the light-dressed potential energy surface of CS2 by coincidence momentum imaging, Chemical Physics Letters, Volume 388, Issues 1–3, 2004, Pages 1-6
2. Akiyoshi Hishikawa, Hirokazu Hasegawa, Kaoru Yamanouchi, Sequential three-body Coulomb explosion of CS2 in intense laser fields appearing in momentum correlation map, Chemical Physics Letters, Volume 361, Issues 3–4, 2002, Pages 245-250,
3. Tomoyuki Endo et al, Selective bond breaking of CO2 in phase-locked two-color intense laser fields: laser field intensity dependencePhys. Chem. Chem. Phys., 2017, 19, 3550
4. Xiao Wang et al , Coulomb explosion of CS2 molecule under an intense femtosecond
5. laser field, 2016 Chinese Phys. B 25 053301

We are grateful to the reviewer for drawing our attention to the previous literature on NIR induced CEI or CS_2 and CO_2. As stated above, the introduction has been redrafted to include these related references.

"While the NIR-induced dynamics of CS2 have been studied extensively [21–23], as have those of isovalent CO2 [24–26], the present work represents the first application of time-resolved CEI to the UV-induced dynamics of CS2."

6. Guillemin, R., Decleva, P., Stener, M. et al. Selecting core-hole localization or delocalization in CS2 by photofragmentation dynamics. Nat Commun 6, 6166 (2015).

As discussed above, we now refer to this paper in the manuscript.

Minor comments:
- Typo in the first paragraph of the introduction: should be sensitive instead of sensitivity
We are grateful to the reviewer for catching this minor error. The text has been updated accordingly.

- Typo in the second paragraph of page 5: Supplementary Material
This has been corrected in the manuscript.

- I suggest to add a reference to table S1 in the caption of fig. 4

We thank the reviewer for suggesting this clarification and have added the following text to the caption of Figure 4. - “Values of R_crit for the different charge transfer processes were calculated using the classical over-the-barrier model and are shown in Table S1 in the Supplementary Information”

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

I read the answer to my comments, the revised manuscript and supplementary information. I thank the authors to address the point I believed were necessary before publication.

I particularly appreciate the effort to clarify the goal of the work and to test the different parameters in the simulations.

As a remark, I do not agree with the authors that high-accuracy electronic structures or dynamics calculations would be prohibitive for this system. Additionally, I do believe that even if the goal is to probe the purely nuclear dynamics, the role of the populated electronically excited states cannot be left out, as different states lead to different nuclear dynamics. However, the authors now made successfully clear in the manuscript how these points are beyond the scope of the present work.

For these reasons, I believe that the manuscript is now publishable in Communications Physics as it is in the current form.

Reviewer #2 (Remarks to the Author):

The authors have fully addressed my concerns and comments.
The new 1D plots are a convincing extraction of the 2D data. Only thing left: I suggest to add error bars and identify blue and red curves in fig. 3 (i) and (j). Otherwise it might be confusing that the integration over positive components leads to an overall negative signal at long time delays (red curve in (i) at 1.5 and 2.8ps).

We address the comments of the reviewers below where our response is in blue, quotes from MS in green and highlighted changes/additions to MS in red.

Reviewer 1

I read the answer to my comments, the revised manuscript and supplementary information. I thank the authors to address the point I believed were necessary before publication.

We are glad the reviewer is satisfied with the responses and the requested changes to the manuscript

I particularly appreciate the effort to clarify the goal of the work and to test the different parameters in the simulations.

We believe this request from the reviewer including the further analysis of effects of testing variable parameters in the simulations significantly strengthened the manuscript.

As a remark, I do not agree with the authors that high-accuracy electronic structures or dynamics calculations would be prohibitive for this system. Additionally, I do believe that even if the goal is to probe the purely nuclear dynamics, the role of the populated electronically excited states cannot be left out, as different states lead to different nuclear dynamics. However, the authors now made successfully clear in the manuscript how these points are beyond the scope of the present work.

Overall, we agree with the reviewer that the role of individual electronic states ultimately cannot be left out and we are hopefully developments in Coulomb explosion imaging combined with x-ray photoelectron spectroscopy may provide these exact details.

For these reasons, I believe that the manuscript is now publishable in Communications Physics as it is in the current form.

We thank the review for their positive assessment of the manuscript and recommendation it be published as is.

Reviewer 2

The authors have fully addressed my concerns and comments.

We are delighted that the reviewer is satisfied with the changes to the revised manuscript.

The new 1D plots are a convincing extraction of the 2D data. Only thing left: I suggest to add error bars and identify blue and red curves in fig. 3 (i) and (j). Otherwise it might be confusing that the integration over positive components leads to an overall negative signal at long time delays (red curve in (i) at 1.5 and 2.8ps).

The requested inclusion of error bars as well as labels has been implemented in a revised Figure 3. The error bars were obtained via bootstrapping analysis.