

jz-2023-01447g.R1

Name: Peer Review Information for "Time-Resolved X-Ray Photoelectron Spectroscopy: Ultrafast Dynamics in CS₂ Probed at the S 2p Edge"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The manuscript represents a large-scale cooperation of multiple groups on the photodissociation dynamics of CS₂. Experiments were carried out at the FLASH free electron laser in Hamburg, using 180 eV radiation to probe the dynamics at the sulfur 2p edge. CS₂ is a well-studied molecule, so this work seems to be meant as a proof-of-principle example that S-edge XPS in combination with theory is well suited to disentangle the excited state processes in a small molecule with a dynamics that is complicated by coupling between the electronic and nuclear degrees of freedom. The experiments are accompanied by quantum dynamics calculations that are essential to assign the various contributions in the time-resolved XPS. The results represent an interesting piece of science, using a rather novel experimental approach and high-level theory. The manuscript will be of interest to a significant part of the readership of JPCL and should be published. I only have a few small remarks that the authors might follow.

1. To my mind the experimental time constants in the manuscript are given with an unreasonable accuracy, for example the IRF might better be given as 120+/-50 fs rather than 117+/-49. An excited state lifetime of 830+/-200 fs and rise times of 500+/-280 fs and 1200+/-240 fs might be more appropriate too.
2. The deviation between excited state decay and product increase is attributed to a “..coherent superposition of compound scattering resonances..” Here, I would appreciate some more detail. The computations in the SI seem to indicate a bifurcating excited-state wavepacket, is that part of the explanation? Without having read the previous papers, I am a bit at a loss here.
3. Figure 2c: The label at the right-hand side of the figure are too small and should be increased.
4. And finally, given the large number of authors it would be interesting to get information on the individual contributions in the SI.

Reviewer: 2

Comments to the Author

This work represents a good exercise to apply complex experimental techniques, such as time-resolved X-ray photoelectron spectroscopy, involving UV-pump X-ray-probe pulses and photoelectron imaging detection, for the elucidation of the complex dynamics of gas phase photodissociation of carbon sulfide (CS₂) after excitation at around 200 nm by probing the S2p edge. However, the results obtained are really very discouraging. There is nothing new or new insights provided by these experiments to the already well-known dynamics of photoexcited CS₂ at around 200 nm, even including the theoretical simulations. It seems it is the wrong technique chosen to study the time-resolved dynamics of this molecule. This kind of experiments are actually becoming routine nowadays (involving large scale facilities and a number of researchers) and all of them lack of providing new insights on the molecular

dynamics studied due to the inherent limitations of the techniques chosen. There is in general very low time resolution attained here and the measurements lack of enough contrast and significance. Therefore, I suggest rejection of this article in JPC Lett and encourage the authors to submit to the family of JPC, most probably to JPC A, after revising the manuscript to improve its presentation and readability.

Reviewer: 3

Comments to the Author

The paper by Gabalski et al. reports time-resolved X-ray photoelectron spectroscopy of photoexcited CS₂ molecules probed at the S 2p edge. The authors investigate the ultrafast dynamics by monitoring spectral shifts of S 2p photoelectron peaks in the course of photodissociation. Although the energy resolution was not enough to resolve each S 2p photoelectron peak associated with photofragments(S, CS) as well as the ground and photoexcited CS₂, the transient spectral changes were identified. The transient peaks were assigned by theoretical calculation based on ab initio multiple spawning. By fitting the observed temporal curves with functions based on a kinetic model, the authors obtained a decay time of the excited state signal and a rise time of the photoproduct signals, which are roughly consistent with those obtained in previous studies.

Chemical shifts of inner-shell photoelectrons of atoms within molecules sensitively reflect the bonding states around the atoms. This is in marked contrast to valence photoelectron spectroscopy which is more sensitive to changes in electronic states. Thus, time-resolved inner-shell photoelectron spectroscopy is becoming an important technique since it provides information that cannot be obtained by other methods including valence photoelectron spectroscopy. What Gabalski et al. carried out is such an inner-shell probe for ultrafast dynamics of CS₂. The experimental results are carefully analyzed and their interpretation by the theoretical calculation is reasonable. The manuscript is certainly suitable for publication, but it is not clear to me whether the manuscript should be published in JPCL. I do not feel that the work advances our understanding of the complex multi-channel dynamics of CS₂ by providing more significant information than what has been obtained in the previous studies. In the present form, I think that it is perhaps better suited to JPCA or JCP rather than JPCL.

There are a couple of minor points that the authors should consider before publication.

Comment1

Photodissociation of CS₂ in the 1B₂ state is known to produce singlet S(1D₂) and triplet S(3P) fragments, and the yield in the triplet channel is larger than the singlet one. However, the authors take only the singlet channel into account for the simulation in Fig. 2. The authors should mention more clearly how it is reasonable to compare it with experimental results which would have the larger triplet contribution. Could this be the primary discrepancy of timescale between the simulation and experiment?

Comment2

Page 10, # 4-11

The authors describe stretched CS with a bond length of $R_{CS} = 1.85 \text{ \AA}$. However, in ref.38, a vibrational distribution of $v=0-9$ is related to a diatomic CS, not stretched CS₂. The authors should explain more clearly the relation between the stretched CS₂ and CS fragments.

Typos

Supporting Information P6 line 3

Figure number is missing.

Supporting Information P13 line 6

A_{beat} and ϕ_{beat} are not used in eq. S3.

Reviewer: 4

Comments to the Author

This manuscript reports on an important nascent field, time-resolved XPS for studying chemical transformations. While I am not particularly excited about the choice of molecule, CS₂, I appreciate the need to begin with simple systems before expanding both the capabilities and the complexity of the systems under study. The manuscript is particularly well-written and will serve as a good introduction of the technique to the larger chemical physics community. I strongly recommend publication.

Author's Response to Peer Review Comments:

Prof. Editor, Editor
Journal of Physical Chemistry Letters

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9 July 2023

Dear Prof. Editor,

We thank the four reviewers for their helpful comments and feedback. We have made revisions accordingly and believe they have strengthened the presentation and focus of this manuscript as well as allowed for correction of some small errors. We highlight in our response to the referees that this work is primarily the presentation of a novel time-resolved technique, namely time-resolved x-ray photoelectron spectroscopy. The choice of CS₂ as an initial application was due to its long-standing status as a benchmark system whose dynamics are well-studied and generally understood. We have more strongly emphasized this fact throughout the manuscript.

We address the comments of the reviewer below where our response is in blue, quotes from MS in green and highlighted changes/additions to MS in red. Additionally, we have addressed the editorial concerns regarding the formatting of the manuscript. One reviewer suggested the inclusion of an author contributions statement, which has been added to the current SI.

Editorial changes

1) TOC Graphic: Provide a TOC image per journal guidelines (2 in x 2 in; on the same page as the abstract) with the heading “TOC Graphic” above the graphic. The graphic should be in the form of a structure, graph, drawing, photograph, or scheme—or a combination. Non-scientific cartoon-like images or caricatures are discouraged.

2) References: In both the main file and the supporting information, fix the style of all references to use JPCL formatting (check all references carefully). ***JPCL Letters reference formatting requires that journal references should contain: () around numbers, author names, article title (titles entirely in title case or entirely in lower case), abbreviated journal title (italicized), year (bolded), volume (italicized), and pages (first-last). Book references should contain author names, book title (in the same pattern), publisher, city, and year. Websites must include date of access.

We have formatted all references in both the main text and the SI to conform to JPCL format.

3) Author Affiliations: Please include postal codes/country in the author affiliations in the publication file(s).

We have added postal codes and countries to the author affiliations where they were previously missing.

4) Supporting Information: Please number SI pages in the following format: “S1, S2...”

We have changed the page numbering in the SI to adopt this standard format.

Reviewer 1

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

We thank the reviewer for their very positive assessment of our manuscript and have outlined in detail responses addressing their minor points below.

Comments:

The results represent an interesting piece of science, using a rather novel experimental approach and high-level theory. The manuscript will be of interest to a significant part of the readership of JPCL and should be published.

We are delighted that the reviewer noted our combination of high level *ab initio* theoretical simulations with time-resolved X-ray photoelectron spectroscopy. To our knowledge, this represents the first study of this kind and hopefully will prove useful to the JPCL readership.

1. To my mind the experimental time constants in the manuscript are given with an unreasonable accuracy, for example the IRF might better be given as 120 ± 50 fs rather than 117 ± 49 . An excited state lifetime of 830 ± 200 fs and rise times of 500 ± 280 fs and 1200 ± 240 fs might be more appropriate too.

We thank the reviewer for pointing out the unreasonably high level of precision in our reported time constants. We have made adjustments to the level of significant figures in each of these instances to be more in agreement with their associated uncertainties in both the text and the figures. Examples of such changes in the main text can be found on Page 11: “The Franck-Condon excited-state $^1\Sigma_u^+$ lifetime of $\tau_{\text{exc}} = 830 \pm 200$ fs measured here is in good agreement with the results of Bisgaard *et al.*, ...” and “The instrument response function (IRF) was determined [...] to be $\tau_{\text{IRF}} = 120 \pm 50$ fs full width at half maximum (FWHM), ...”

2. The deviation between excited state decay and product increase is attributed to a “..coherent superposition of compound scattering resonances..” Here, I would appreciate some more detail. The computations in the SI seem to indicate a bifurcating excited-state wavepacket, is that part of the explanation? Without having read the previous papers, I am a bit at a loss here.

The UV absorption spectrum of CS_2 around 200 nm is dominated by a vibrational progression (a series of peaks). These peaks, however, are not stationary eigenstates since we know that CS_2 undergoes predissociation here. As was shown years ago by Mank and Hepburn in Ref. 22, tuning a laser to one of these absorption peaks will lead to emission of S atoms and CS co-fragments. This means that these peaks represent meta-stable states (called predissociation resonances), described as a bound state embedded in a dissociative continuum. The linewidth of the peak is related to the decay lifetime of that particular resonance. From a scattering theory point of view, the problem can be equally understood as a S atom which collides with a CS fragment, forming a meta-stable collision complex (this is the scattering resonance) which then emits a UV photon to the ground state. This is exactly the time-reversed description of the photodissociation problem described here and is an equally valid description of the dynamics. In other words, the basis set for describing the quantum dynamics can be chosen to be the separated scattering states.

A femtosecond laser has a broad coherent bandwidth which therefore prepares a coherent superposition of these resonances which will simultaneously beat against each other and decay. This

is a perfectly correct and alternative description of this experiment. This scattering theory perspective was previously described in detail for the analogous problem of pre-dissociation in the Iodine Bromide molecule (Shapiro et al. JChemPhys 1999, Ref. 39).

These scattering (predissociation) resonances are complex in that they correlate to multiple open channels: two different S atoms (singlet and triplet) and a range of CS product quantum states. The 'bifurcation' is therefore contained in the detailed nature of these complex resonances and is not easily pictured in this language. Semi-classical wavepacket dynamics, however, can give a mechanistic picture of the dynamics. Kinetic models applied to these experiments (or theory) will yield a simple parameter related to the decay of the excited state but will not include the coherent beating between the prepared states (resonances).

3. Figure 2c: The label at the right-hand side of the figure are too small and should be increased.

We have made the appropriate adjustment to the text size in this figure to increase its legibility.

4. And finally, given the large number of authors it would be interesting to get information on the individual contributions in the SI.

An author contributions statement has been added to the SI and contains the following information. If the editor would prefer this located elsewhere we are happy to rearrange this section.

"R.F. conceived the experiment, the plan for which benefited from further input from F.A., G.B., T.D., B.E., D.R. and M.S.. The electron spectrometer was prepared by B.E., A.T.N., C.C.P., C.P. and the photon spectrometer by G.B.. The optical laser setup was constructed by N.E. with further input from R.F.. The experiment was conducted onsite by G.B., H.B., N.E., B.E., D.G., E.G., S.K., A.T.N., C.C.P., C.P., A.Rod., A.Rou., A.Si., with online participation in the experiment by all coauthors. The experiment data was analyzed by F.A., M.Br., I.G., J.U. and the theoretical simulations performed by S.N., M.S. and I.S. Finally, F.A., I.G., R.F, D.R., M.S. and A.St. interpreted the results and wrote the manuscript with input from all the authors."

Reviewer 2

Recommendation: While the work is good and publishable, a more appropriate journal is recommended such as The Journal of Physical Chemistry A

We thank the reviewer for their assessment that the work is good and publishable but respectfully disagree about the importance of the work. Both reviewers 1 and 4 feel that this work is of broad appeal to the physical chemistry community and have "strongly recommended publication." The work represents an important first step in combining time-resolved inner-shell photoelectron spectroscopy with high level *ab initio* simulations, including full simulation of the time-dependent observables.

Comments:

This work represents a good exercise to apply complex experimental techniques, such as time-resolved X-ray photoelectron spectroscopy, involving UV-pump X-ray-probe pulses and photoelectron imaging detection, for the elucidation of the complex dynamics of gas phase photodissociation of carbon sulfide (CS₂) after excitation at around 200 nm by probing the S2p edge. However, the results obtained are really very discouraging. There is nothing new or new insights provided by these experiments to the already well-known dynamics of photoexcited CS₂ at around 200 nm, even including the theoretical simulations.

We regret that we did not clearly convey the main focus of this letter. Our aim was to use the well-known UV excited state dynamics of CS₂ as a means to characterize/validate a new technique: TRXPS. We have added clarifying phrases and rewording throughout the abstract, introduction, and conclusion to emphasize the fact that we intended this work to be a proof-of-concept study of the TRXPS technique for understanding multimodal vibrational coupling, non-adiabatic dynamics, and multiple final product channels and thus chose the well-studied CS₂ system as an ideal model system which exhibits these properties.

In the abstract: “We present results from a joint experimental and theoretical TRXPS study into the well-characterized ultraviolet photodissociation of CS₂, a prototypical system for understanding non-adiabatic dynamics.”

In the introduction: “Here we present results of a joint theoretical-experimental proof-of-concept study of the sensitivity of the time-resolved X-ray photoelectron spectroscopy (TRXPS) technique to the complex multi-channel UV photodissociation of carbon disulfide (CS₂) probed via photoionization above the sulfur 2p edge.”

In the conclusion: “... Quantification of reaction timescales using TRXPS and comparison to prior valence studies reveals the complex nature of this reaction and the inadequacies of some kinetic models commonly employed to describe it. These results demonstrate the sensitivity of the TRXPS technique to multimodal molecular motion in the gas phase more generally, crucially including both signatures of the transient bound excited state and the vibrational states of the photoproducts in addition to providing a multifaceted picture of the reaction kinetics. In the case of CS₂,...”

It seems it is the wrong technique chosen to study the time-resolved dynamics of this molecule. This kind of experiments are actually becoming routine nowadays (involving large scale facilities and a number of researchers) and all of them lack of providing new insights on the molecular dynamics studied due to the inherent limitations of the techniques chosen.

We disagree with the referee’s assessment that time-resolved X-ray photoelectron spectroscopy is becoming routine nowadays. As also remarked by reviewer 4 - “This manuscript reports on an important nascent field, time-resolved XPS for studying chemical transformations.” Our results represent one of the first studies exploiting this technique alongside side-by-side comparison with *ab initio* dynamics simulations with the full computation of experimental observables. Many different types of experiments are conducted at free-electron laser facilities, but this type of energy and time-resolved inner-shell photoelectron spectroscopy on isolated gas-phase molecules is yet to become commonplace.

We furthermore note that our work presents new insights into the sensitivity of the TRXPS technique to complex multimodal predissociation dynamics that have not yet been proven. We acknowledge in the third paragraph of our introduction the groundbreaking progress made by a handful of previous experiments using atomic site-specific probes. The work from Brausse *et al.* and Allum *et al.* (Refs. 18 and 19) explored the prompt photodissociation dynamics of iodoalkanes via probes at the I 4d edge, but these reactions generally do not exhibit large-amplitude motion in the excited state prior to dissociation. The work of Leitner *et al.* in Ref. 17 explored the coordination chemistry and sequential dissociation of Fe(CO)₅ into Fe(CO)₄ and Fe(CO)₃ by probing above the Fe 3d edge, but this experiment did not observe signatures of the bound excited Fe(CO)₅ molecule. The work by Mayer *et al.* in Ref. 20 observed spectroscopic signatures of the excited state dynamics and relaxation back to the hot ground state of thiouracil via TRXPS above the sulfur 2p edge, but this reaction does not exhibit dissociation into multiple product channels.

Our proof-of-concept TRXPS experiment provides three key insights that each of these other experiments lack in some fashion. (1) Our experiment observed excited-state chemical shifts in the bound CS₂ molecule that decayed for several hundred femtoseconds as the molecule dissociated. The observation of spectral signatures of both the predissociative excited state and multiple rising product populations demonstrates the suitability of TRXPS to completely track reaction dynamics as they unfold. (2) Both our experimental data and our *ab initio* calculations of fragment spectra demonstrate that the sulfur 2p core-level chemical shift is highly sensitive to the vibrational state of the diatomic CS fragment. While we cannot yet conclude that the sensitivity of core-level chemical shifts to vibrational state is a general feature of polyatomic fragments, we would suggest that its observation here is an important first step for the TRXPS technique. (3) The comparison between our measured excited-state decay lifetime and product rise times (which agree well with many prior measurements) do not lend themselves easily to a kinetic description of this reaction. The XPS signal of the excited state of CS₂ and the signals from its S and CS photoproducts are well-separated spectrally, which is a feature not found in prior valence photoelectron spectroscopy studies of this molecule such as the one performed by Karashima *et al.* in Ref. 10. This suggests that TRXPS may be uniquely suited to explore the non-kinetic characteristics of photochemical reactions.

Therefore, I suggest rejection of this article in JPC Lett and encourage the authors to submit to the family of JPC, most probably to JPC A, after revising the manuscript to improve its presentation and readability.

We respectfully disagree with the reviewer regarding publication in JPC Lett. As noted by both reviewers 1 and 4 this work is of considerable interest to the physical chemistry and chemical physics community. In particular, we highlight the response of reviewer 4 - "The manuscript is particularly well-written and will serve as a good introduction of the technique to the larger chemical physics community. I strongly recommend publication."

Reviewer 3

Recommendation: Reconsider as an article in The Journal of Physical Chemistry A/B/C.

Similarly to our response to reviewer 2, we respectfully disagree about the importance and general interest of the current work.

Comments:

The paper by Gabalski *et al.* reports time-resolved X-ray photoelectron spectroscopy of photoexcited CS₂ molecules probed at the S 2p edge. The authors investigate the ultrafast dynamics by monitoring spectral shifts of S 2p photoelectron peaks in the course of photodissociation. Although the energy resolution was not enough to resolve each S 2p photoelectron peak associated with photofragments(S, CS) as well as the ground and photoexcited CS₂, the transient spectral changes were identified. The transient peaks were assigned by theoretical calculation based on *ab initio* multiple spawning. By fitting the observed temporal curves with functions based on a kinetic model, the authors obtained a decay time of the excited state signal and a rise time of the photoproduct signals, which are roughly consistent with those obtained in previous studies.

Chemical shifts of inner-shell photoelectrons of atoms within molecules sensitively reflect the bonding states around the atoms. This is in marked contrast to valence photoelectron spectroscopy which is more sensitive to changes in electronic states. Thus, time-resolved inner-shell photoelectron spectroscopy is becoming an important technique since it provides information that cannot be

obtained by other methods including valence photoelectron spectroscopy. What Gabalski et al. carried out is such an inner-shell probe for ultrafast dynamics of CS₂. The experimental results are carefully analyzed and their interpretation by the theoretical calculation is reasonable. The manuscript is certainly suitable for publication, but it is not clear to me whether the manuscript should be published in JPCL. I do not feel that the work advances our understanding of the complex multi-channel dynamics of CS₂ by providing more significant information than what has been obtained in the previous studies. In the present form, I think that it is perhaps better suited to JPCA or JCP rather than JPCL.

We are delighted that the reviewer noted the importance of the technique of time-resolved inner-shell photoelectron spectroscopy and also noted the careful analysis of our experimental results and our reasonable interpretation of the data in light of simulated spectra. We stress that this work, as noted by reviewer 4, is a first step in an "important nascent field, time-resolved XPS for studying chemical transformations."

Again, we regret that we did not clearly convey the main focus of this letter. Our aim was to use the well-known UV excited state dynamics of CS₂ as a means to characterize/validate a new technique: TRXPS. We aimed to showcase the technique's ability to extract information inline with the previous literature but also note that we do provide new physical insight regarding the sensitivity of inner-shell chemical shifts to the photoproduct vibrational distributions. Our *ab initio* calculation of the spectroscopic observables of these fragments indicates that the S 2p binding energy of the CS fragment is highly sensitive to this bond length, as demonstrated in Figure 3 of the main text. The sensitivity of our observable to this aspect of the photodissociation of CS₂ is a key finding of this work.

There are a couple of minor points that the authors should consider before publication.

We thank the reviewer for helping to clarify the points below and catching several small typos. The responses are outlined below in detail.

Comment1

Photodissociation of CS₂ in the 1B₂ state is known to produce singlet S(1D₂) and triplet S(3P) fragments, and the yield in the triplet channel is larger than the singlet one. However, the authors take only the singlet channel into account for the simulation in Fig. 2. The authors should mention more clearly how it is reasonable to compare it with experimental results which would have the larger triplet contribution. Could this be the primary discrepancy of timescale between the simulation and experiment?

Since the dynamics simulations were performed exclusively on the singlet manifold, this precludes the ability of the calculated spectra to fully reproduce all the experimental signals. However, if dissociation on the triplet manifold is relatively prompt (which we suggest is reasonable given that the energetically close triplet curves are purely repulsive), it would be assumed that the main shortcomings of the simulation would be i) an absence of the spectral signature of the ³P S atom product, ii) an excited state lifetime that would be too long, since a decay pathway is absent, and iii) an incorrect rise time in the CS product yield, since all CS product comes exclusively from the singlet channel.

However, we still see reasonable agreement with experiment given that:

1. ³P S atom ionization channel has strong overlap with the CS and ¹D S atom ionization channels, and while clearly present in the total experimental signal, it is difficult to uniquely identify.

2. Simulation should, if the initial conditions are correctly accounted for (as discussed below) quantitatively reproduce FC region dynamics and structural relaxation within CS₂ singlet manifold. Neither of these ionization channels overlap with the predicted location of the dominant ³P S ionization channels.
3. In general, the short-time dynamics should be predominantly due to dynamics on the singlet manifold and the simulation is particularly helpful in identifying those regions corresponding to dynamics within the bound CS₂ vs. the CS fragment, the latter being common to both the singlet and triplet dissociation channels. The primary difference at longer times is a quantitatively inaccurate prediction for the timescale of the rise of CS products (and/or an incorrect description of the overall temporal profile), as well as the absence of the ³P ionization channel at (predicted) lower kinetic energies. Thus, while there is some disagreement expected in the temporal evolution of the signal, this does not negate the fact the simulation is essential for the assignment of spectral features to molecular electronic and nuclear characters.

As for the primary discrepancy between theory and experiment, only a more comprehensive simulation can answer that question with certainty. That said, in the paper we suggest that a proper description of the initial conditions is of comparable importance, as even without the triplet decay mechanism, the singlet CS₂ lifetime is still simulated to be shorter than what is observed in the experiment. Assuming prompt decay within the triplet manifold, the opposite would be expected: that the absence of an additional rapid decay pathway would lengthen the CS₂ excited state lifetime. As stated in the manuscript, we assign this discrepancy to a calculated wave packet with too much internal energy given the approximate manner in which the pump process is simulated. Any future simulations would therefore need to model the pump process more rigorously in order to reproduce the temporal evolution of the wave packet, in addition to the inclusion of coupling to the triplet manifold.

We have added the following text to more explicitly detail this shortcoming in the simulation:

“While the simulated TRXPS is essential for assigning spectral features to particular atomic and molecular species, the absence of a triplet dissociation channel in the simulated results will result in a different temporal evolution between the measured and calculated spectra. In addition to lacking an ionization signal corresponding to ³P atomic S product, and assuming that the dissociation is relatively prompt following intersystem crossing, the simulation will exhibit i) a slower rise in the CS product formation, and ii) a longer CS₂ lifetime. “

Comment2

Page 10, # 4-11

The authors describe stretched CS with a bond length of $R_{CS} = 1.85$ Ang. However, in ref.38, a vibrational distribution of $v=0-9$ is related to a diatomic CS, not stretched CS₂. The authors should explain more clearly the relation between the stretched CS₂ and CS fragments.

We thank the reviewer for seeking clarification on this point regarding the stretched CS fragment. The spectral region in question in this section of the manuscript is in fact associated with the stretched diatomic CS fragment, and not the CS₂ molecule with stretched bond lengths as the reviewer suggests. As the dissociation progresses, diatomic CS fragments are produced by both the S atom singlet and triplet channels (see Refs. [23-24] for measured vibrational distributions), which are thereby produced with a distribution of bond lengths as indicated by Ref. [38]. As mentioned above, our *ab initio* calculation of spectroscopic observables shows that the sulfur 2p XPS signal of the CS fragment is highly sensitive to its bond length, and is a key finding of our work.

We have added the following clarifying wording to the sentence in question on page 10 of the text:
“The mid-eKE region bounded by the red dashed lines is associated primarily with the stretched diatomic CS fragment, distributed broadly between the equilibrium length out to a bond length of $R_{CS} \sim 1.85 \text{ \AA}$.”

Typos

Supporting Information P6 line 3

Figure number is missing.

We thank the reviewer for catching this minor typo. We have corrected the Supporting Information text as follows - “Note that the eKE shift employed for static S-atom spectra in Figures 3 (main text) and S4 was determined from cc-pCVTZ / EOM-CCSD calculations performed using the QChem package.”

Supporting Information P13 line 6

A_{beat} and ϕ_{beat} are not used in eq. S3.

We apologize for this inconsistency due to an incorrect rearrangement of the descriptions of the various fits during our editing process, and have corrected the text in the SI, P13 line 6 (now on page S14 due to reformatting) as follows:

“Here A_{exc} and τ_{exc} are the amplitude and lifetime of the excited state signal, ~~A_{beat} and ϕ_{beat} are the amplitude and phase of the quantum beat~~, and A_{prod} and τ_{prod} are the amplitude and lifetime of the exponential rise of photoproduct signal.”

Reviewer 4

Recommendation: This paper represents a significant new contribution and should be published as is.

We thank the reviewer for identifying the significance of our manuscript.

Comments:

This manuscript reports on an important nascent field, time-resolved XPS for studying chemical transformations. While I am not particularly excited about the choice of molecule, CS₂, I appreciate the need to begin with simple systems before expanding both the capabilities and the complexity of the systems under study. The manuscript is particularly well-written and will serve as a good introduction of the technique to the larger chemical physics community. I strongly recommend publication.

We appreciate the kind words of the referee with respect to the clarity of the manuscript and it serves as a good introduction of the technique to the larger chemical physics community as well as their strong endorsement for publication.

We believe we have addressed the concerns of the reviewers, as well as the editorial office, and hope that this manuscript is now suitable for publication in J. Phys. Chem. Lett. Please do not hesitate to contact us with any further concerns or questions.

Sincerely,

Ian Gabalski, Felix Allum, Albert Stolow, Michael Schuurman and Ruaridh Forbes (on behalf of all authors).