October 15, 2024

Dear Associate Editor,

Professor Wolfgang E. Ernst

Article **CP-ART-09-2024-003687**

Enclosed please find our **revised** research article No. **CP-ART-09-2024-003687** entitled ‘**Experimental and theoretical study of the Sn – O bond formation between atomic tin and molecular oxygen’** for the *Physical Chemistry Chemical Physics*. All changes made to the text during revision were highlighted in yellow.

We sincerely thank the editor and reviewers for taking the time to review our manuscript and providing constructive feedback to improve our manuscript. We have revised the manuscript accordingly by following the reviewers’ suggestions. Below are the original comments from the reviewers (*italics*) and our point-by-point response:

**Referee 1:**

*Comments to the Author  
This is an interesting paper that could find its place in PCCP. However, the authors should consider the following recommendations in a revised manuscript:*

***a) I consider Fig. 1 not suitable for this paper. Why do the authors show structures of hydrides in ground and excited states when this paper is clearly only on oxides? This is just some unnecessary information that doesn't add to the story of this paper.***

**Response:**

We agree with Referee, Figure 1 was removed from the manuscript.

***b) Figure 3 should be shown as a stick or bar diagram. The points should not be connected by straight lines.***

**Response:**

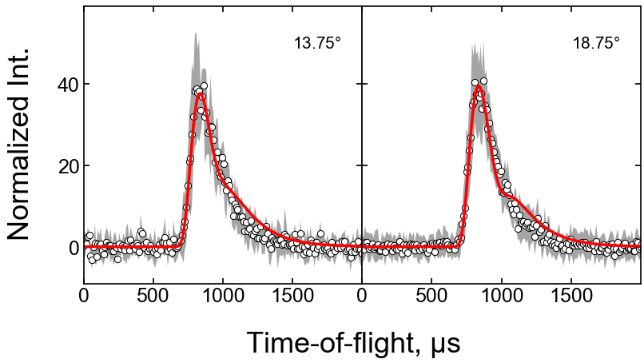
In the revised version type of the diagram in Figure 3 was changed to a bar diagram.

***c) In Figure 4b, the simulations clearly show shoulders on the main peaks. This behavior is not seen in the experimental data. Can the authors please explain?***

**Response:**

We think that several factors can account for that:

1. This is a heavy atom system and simulations that reproduce experimental data in all details may not be possible;
2. Likely, the shoulder was ‘smoothed’ during recording due to the velocity variations of primary and secondary beams during the experiments. See below the figure of two main peaks with grey areas represent the error bars of each TOF point (red line – simulation, white points – averaged experimental) – red line is inside error bars limits;



1. Contributions of channels with different spin-orbit levels of tin may also influence the final recorded shape of TOFs, however, determining their exact branching ratios is out of the scope of this publication. In general, we think that it might be possible to introduce a three-channel fit by treating every channel with different spin-orbit tin levels as a separate channel and adjusting their branching ratios and parameters till a better-looking TOF fit without a shoulder is achieved. However, we are afraid in such a way we would step on the grounds of ‘fitting for the sake fitting’.

We also would like to highlight that our current simulation successfully fits not only the most intense TOF around CM, but also at the lowest recorded angle (8.75°) and at the high angle of 48.75° with the lowest recorded intensity.

***d) Not sure what the "donut" in Fig. 5c indicates. No scales, just color coded. Can the authors be more quantitative?***

The reference scale was added to the flux contour map (Fig. 5c) and the probability was normalized to 1 on the color bar.

***e) I refuse to look at Fig. 6. Why do the authors think that such a figure is acceptable for publication? The authors need to provide a figure that is meaningful and legible. If needed, nobody stops them from splitting the information up into several figures.***

Fig. 6 was updated in the revised manuscript. Only intermediate structures (without distances and angles) were kept, while the figure with structures of transition states, intersystem crossings (MSX), and intermediates was moved to SI as Figure S2.

**Reviewer 2:**

*Comments to the Author.*

*This is a very impressive paper describing the Sn + O2 reaction using state of the art experiment combined with top level theory.  I am not an expert for evaluating the theory components but judging from the track record of this team I have all confidence that the theory is just as reliable as experiment.  While the introduction is lengthy, I appreciated the overview and perspective and would not suggest making it shorter.  The experimental description, on the other hand, is quite compact, but in line with more extensive descriptions by these authors.  As one would expect from this quite difficult heavy atom system, a unique mechanism consistent with the observed energy release and angular distributions is not possible.  The authors did narrow down the possibilities considerably, in any case.  The paper is well-written and convincing (as far as possible) and the figures are all useful and necessary****.  In my opinion the references can be condensed as there are numerous self-citations that are not clearly justified in the text.*** *The authors can be trusted to act on this properly.  I highly recommend publication in PCCP.*

**Response:**

Citations [52–54] from the original version were removed in the revised version.

Sincerely,

Ralf

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