Response to the reviewer 2

In this work, Chen, Qin et al. performs a systematic and exhaustive quantum chemistry study on the reaction of the collision reaction between P and molecular oxygen giving rise to O and PO with relevance in the Earth's atmospheric chemistry of phosphorus and its interstellar chemistry. While previous theoretical studies focused on providing "static information", in this case, the authors performed both semi-classical and quantum dynamics simulations to provide with time-dependent properties. The quality of the study is high and the methods and techniques are the most state-of-the-art ones for this type of problems. The presentation of the manuscript is also very clear, systematic and precise.

Reply: We thank the reviewer for their comments which we address below.

Specific Comments:

#Comment 1: Even though in the title is it stated "… implication for atmospheric modelling", there is no much discussion on how the new data obtained from the dynamics simulations would impact the chemistry in the atmosphere and interstellar media of the studied system. More details and illustrative examples would help to enhance the scientific significance of the work.

Reply: We thank the reviewers for this important point. We have added the relevant descriptions, as shown below:

Lines 439 to 463 - '**6 Atmospheric Implications**

The ablation of IDPs in the upper atmosphere (mainly at heights between 70 and 110 km) of terrestrial planets delivers about 6,200 kg yr^{-1} ablated phosphorus to the atmosphere (Carrillo-Sánchez et al., 2020), where the temperatures ranging from below 100 to over 2500 K (in ablation IDPs). Several reaction networks of meteor-ablated phosphorus in the Earth's upper atmosphere (Douglas et al., 2019; Douglas et al., 2020; Plane et al., 2021) indicate that the initial oxidation of P will proceed through the successive oxidation by O_2 to produce OPO (i.e. reactions R1 and R2). The oxidation by O_3 is not significant because O_2 is 10^5 times more abundant than O_3 at this altitude. Also, OPO is likely dissociated into PO and P as a result of hyperthermal collisions with air molecules (Carrillo-Sánchez et al., 2020). Therefore, the $P + O_2 \rightarrow O + PO$ reaction may occur throughout the upper mesosphere and thermosphere. Our rate constants are fitted by sufficient data below 5000

K, which is appropriate for most altitude of the Earth's atmosphere and can be used to model its phosphorus chemistry.

A recent study developed a reaction network of phosphorus atmosphere chemistry (Plane et al., 2021), including the possible routes from $P + O_2 \rightarrow O + PO$ to the stable reservoirs (H_3PO_3 and H_3PO_4). Subsequently, they incorporated the rate constants of the associated reactions into the Whole Atmosphere Community Climate Model from the US National Center for Atmospheric Research (Gettelman et al., 2019), and then explored the vertical profiles of the P-containing species and the global mean P deposition flux. Also, they estimated that the fraction of the ablated phosphorus forming bioavailable metal phosphites was 11%.

One of our concerns is that the theoretical predicted rate constants of $P + O_2 \rightarrow O + PO$ diverge from experimental result at 200 K, which is about the typical temperature of the upper mesosphere and lower thermosphere. For the reaction with entrance barrier, its rate constant usually has Arrhenius linear behaviour at relative low temperatures. Our QCT and TDWP rate constants, as well as the TST rate constant (Gomes et al., 2022), exhibit highly consistent Arrhenius linear behaviour at relative low temperatures, with slopes close to those of the experimental rate constants at about 300-600 K (Douglas et al., 2019), as shown in Fig. 8 (b). There is reason to believe that the experimental results of 300-600K are very reliable. Whereas, the experimental rate constant at about 200 K seems to be slightly overestimated, so the lifetime of the P atoms in the atmosphere may be a little longer than previously thought (Carrillo-Sánchez et al., 2020). Further experiments for the rate constants at approximately 200 K of $P + O_2 \rightarrow O + PO$ are encouraged in the future.'

Technical Corrections:

#Comment 1: On page 4, equation (1), define R1, R2 and R3.

Reply: Thanks for your advice. We have redefined this equation, as follows:

$$PO_2(X\,^2A_1/^2A') \rightarrow O(^3P) + PO(X\,^2\Pi) \quad \text{R1}$$

$$\rightarrow P(^4S) + O_2(X\,^3\Sigma^-) \quad \text{R2}$$

$$\rightarrow P(^4S) + O(^3P) + O(^3P) \quad \text{R3}$$

#Comment 2: On page 6, line 169, change "…to construct a global the PES…" by "…to construct a global PES…"

Reply: Thanks for your advice. We have removed 'the' in line 169, as follows:

Line 161 - '… to construct a global PES of PO_2'

#Comment 3: In relation to Table 2, please define more clearly the meaning of "ascending ordered energies" and the meaning of the numbers.

Reply: Thanks for your advice. We have rewritten the definition, as follows:

Lines 173 to 175 - 'The final PES was constructed from 6471 *ab initio* energy points, covering an energy range up to 500 kcal/mol above the GM. Table 2 lists the RMSDs between the analytical CHIPR energies and *ab initio* energies in the indicated energy range above the GM and those for the additional energy grids.'

Table 2 The root-mean-square deviations (RMSDs) in the indicated energy range above the GM and those for the additional energy grids.

	N [a]	Max deviation [b]	RMSD [c]	$N_{>RMSD}$ [d]
Energy Range [e]				
10	1560	95.4	24.6	447
20	1892	103.9	23.1	504
40	1986	152.0	24.4	485
60	2039	185.5	29.4	439
80	2131	226.5	37.9	339
100	2231	263.9	52.9	253
200	5911	280.3	84.4	1218
300	6415	319.1	90.1	1441
500	6471	387.9	91.5	1461
Configuration [f]				
GM	1554	79.7	24.5	452
LM	490	71.4	21.4	140
TS1	810	48.6	20.3	292
TS2	405	29.8	10.5	118
TS3	810	34.1	13.4	242
TS4	810	60.8	14.5	188

[a] The number of energy points in the corresponding range. [b] The maximum deviation in the corresponding range, cm^{-1}. [c] The RMSD for the corresponding range, cm^{-1}. [d] The number of energy points with a deviation larger than the RMSD. [e] The indicated energy range above the GM, kcal mol^{-1}. [f] The additional energy grids.

#Comment 4: In Fig. 2, it would help the reader if E_h is defined.

Reply: Thanks for your advice. Since the E_h is first used in the Fig. 1, we have added the corresponding definition on Fig. 1 caption, as follows:

Line 151 – 'Fig. 1 (a) The PECs of $O_2(X\ ^3\Sigma^-)$ and $PO(X\ ^2\Pi)$. The unit of potential energy is the atomic unit (Hartree, E_h).'

#Comment 5: On page 8, line 210, change "Fig. 4(a)" by "Fig. 2(a)".

Reply: Thanks for your advice. We have changed 'Fig. 4(a)' by 'Fig. 2(a)' in line 210 as follows:

Line 199 - 'Fig. 2 (a) presents the channel of an O atom dissociated from $PO_2(X\ ^2A_1)$ …'

#Comment 6: On page 8, line 211, rewrite this sentence since the O atom dissociation indeed requires energy and therefore it is not "barrierless".

Reply: Thanks for your advice. We have removed 'barrierless' in line 211, as follows:

Line 199 - 'Fig. 2 (a) presents the channel of an O atom dissociated from $PO_2(X\ ^2A_1)$ …'

#Comment 7: On Fig. 4 caption, add at the end of the first sentence "(see definition in the text)" referring to the hyperspherical coordinates.

Reply: Thanks for your advice. We have added '(see definition in the text)' on Fig. 4 caption, as follows:

Line 258 - 'Fig. 2 The relaxed triangular contour plot for the ground-state PO_2 in hyperspherical coordinates (see the definition in the text).'

#Comment 8: In the last paragraph of Conclusions, re-formulate the grammar of the sentence "It can also be a reliable component for constructing other larger molecular systems containing PO_2, such as PO_3 and HPO_2 correspond to the reactions R2 and R3 for generating H_3PO_3 in the Earth's atmosphere."

Reply: Thanks for your advice. We have re-formulated the grammar of this sentence, as follows:

Lines 482 to 484 - 'Moreover, this analytical PES of PO_2 can provide reliable two-body fragments and three-body fragment for the construction of PO_3 and HPO_2 PESs using MBE form, so as to carry out dynamic study of reactions R2 and R3, which are also important for generating H_3PO_3 in the Earth's atmosphere.'

#Comment 9: It would also help the reader if Jacobian coordinated are briefly defined.

Reply: Thanks for your advice. We have added the definition of Jacobian coordinate, as follows:

Lines 104 to 105 – 'For example, the $R_{A\text{-}BC}$, r_{BC} and $\gamma_{A\text{-}BC}$ for the A-BC channel of ABC molecular are defined as the distance of the A atom relative to the center-of-mass of BC, the bond distance of BC and the angle between $R_{A\text{-}BC}$ and r_{BC}, respectively.'