

Responses to Referee #1's comments

We are grateful to the reviewers for their professional and helpful comments on our manuscript “**Mechanistic Insights into I₂O₅ Heterogeneous Hydrolysis and Its Role in Iodine Aerosol Growth in Pristine and Polluted Atmospheres**” (MS No.: egusphere-2025-3770). Accordingly, we have carefully revised the manuscript. The point-to-point responses to the Referee #1's comments are summarized below:

Deng et al. presented a theoretical study showing that, under the influence of atmospheric iodine species and pollutants, I₂O₅ hydrolysis can occur more readily at the surface of aqueous aerosols. These physicochemical processes are valuable, as I₂O₅, being a key chemical in the iodine cycling, has a significant impact on both iodine chemistry and the formation of iodine aerosols. Experimental investigation of gas–liquid interfacial reactions is challenging; therefore, the heterogeneous mechanisms revealed by the authors through Ab initio molecular dynamics simulations provide an important advancement of the previous understanding of the atmospheric fate of iodine oxides. This manuscript is thoughtfully prepared, with reliable methods and comprehensive data in both the main text and the supplementary material that support the conclusions. That said, certain aspects could benefit from minor revision, and I recommend publication after the authors have addressed my comments.

Response: Thanks for the reviewer's professional and valuable comments. We have addressed all comments point by point and made the corresponding revisions in the manuscript. The detailed responses are listed as follows.

Major Comment:

Page 3, lines 84-85: It is stated that gas-phase structure optimizations were performed with Gaussian package, yet the species involved are not clearly identified. As I could not find this information in either the manuscript or the SI. If I have overlooked it, please direct me to the relevant section.

Response: We thank the reviewer for the careful review. This suggestion has reminded us of the missing details in the manuscript. In this study, we optimized the gas-phase conformations of the reactants (e.g., I₂O₅, HIO₃, and H₂SO₄) using the Gaussian 16 program (Frisch et al.,

2016). Accordingly, we have added the relevant molecular information in the Methods section in the revised manuscript (Page 3, line 92), as follows:

“The geometries and coordinates of gas-phase molecules (i.e. I_2O_5 , HIO_3 , H_2SO_4 , MA, DMA, and TMA) are provided in Figure S2 and Table S2 in the supporting information (SI), respectively.” in the Quantum Chemistry Calculations section.

For ease of review, we have copied them as follows:

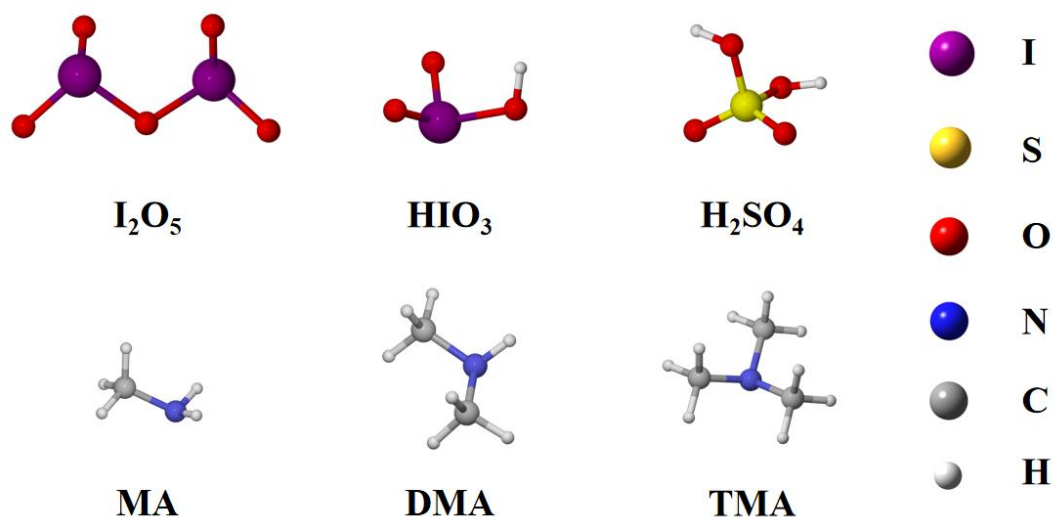


Figure S2. The optimized structures for gas-phase molecules (i.e. I_2O_5 , HIO_3 , H_2SO_4 , methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA)) at the M06-2X/ /aug-cc-pVTZ(-PP) level of theory.

Table S2. Coordinates for all calculated molecules at the M06-2X/aug-cc-pVTZ(-PP) level of theory.

I_2O_5 (Isomer 1)			
O	-0.000013	-0.988788	0.000159
I	1.641204	0.055287	-0.225857
I	-1.641235	0.055311	0.225852
O	2.800249	-1.108887	0.404898
O	1.270721	1.236952	1.040258
O	-2.800236	-1.108859	-0.404989
O	-1.270515	1.236874	-1.040296

HIO ₃			
I	-0.096935	0.013334	-0.244580
O	-0.289743	1.559142	0.594271
O	-1.014657	-1.204758	0.647080
O	1.713186	-0.419126	0.233680
H	1.867280	-0.188774	1.162521
H ₂ SO ₄			
S	0.000001	-0.000003	0.154681
O	0.670149	1.064615	0.826194
O	1.023747	-0.686964	-0.845067
H	1.708834	-0.047610	-1.086390
O	-1.023744	0.686990	-0.845052
H	-1.708821	0.047636	-1.086403
O	-0.670155	-1.064638	0.826162
MA			
N	0.747530	0.000000	-0.120845
H	1.149839	-0.811832	0.328231
H	1.149839	0.811832	0.328231
C	-0.706161	0.000000	0.017785
H	-1.112738	0.876800	-0.483829
H	-1.112739	-0.876799	-0.483831
H	-1.069944	-0.000001	1.050407
DMA			
N	0.000000	0.568475	-0.148304

H	0.000001	1.336588	0.508868
C	-1.204665	-0.224024	0.020309
H	-2.083499	0.413833	-0.056533
H	-1.258202	-0.965087	-0.778566
H	-1.244160	-0.762560	0.977876
C	1.204665	-0.224024	0.020309
H	1.258206	-0.965080	-0.778573
H	2.083499	0.413834	-0.056523
H	1.244156	-0.762568	0.977871
TMA			
N	0.000000	0.000009	-0.389205
C	1.195212	0.683133	0.062542
H	2.079355	0.170403	-0.315039
H	1.202277	1.705136	-0.315089
H	1.260883	0.720681	1.163047
C	-1.189213	0.693506	0.062541
H	-1.187224	1.715614	-0.314877
H	-2.077799	0.188704	-0.315260
H	-1.254710	0.731401	1.163041
C	-0.005990	-1.376629	0.062538
H	-0.892218	-1.885891	-0.314819
H	0.875409	-1.893854	-0.315333
H	-0.006029	-1.452314	1.163040

For the central chemical examined in this work, the I₂O₅ molecule, different isomers are expected to exist. Could the authors clarify why the current structure was selected and on what basis? Moreover, in the introduction the I₂O₅ molecule is described as very stable; does the cited reference pertain to the same structure investigated here? The rationale for the chosen structure should be stated, and the atomic coordinates together with a structural figure are best included in the SI.

Response: The reviewer's comment is professional. In our manuscript, the isomers of I₂O₅ had been already considered before carrying out BOMD simulations. We have surveyed the previously reported structures of I₂O₅ (Kaltsoyannis and Plane, 2008; Khanniche et al., 2016; Kim and Yoo, 2016). Although isomer 2 (Kaltsoyannis and Plane, 2008) is referred to in the Introduction as a stable configuration, our calculations show that isomer 1 (Khanniche et al., 2016) is in fact more stable, with a lower Gibbs free energy. Thus, the most stable isomer 1 was selected for the subsequent BOMD simulations. We have supplemented description for isomers of I₂O₅ in the Methods section as follows (Page 3, line 86):

“The I₂O₅ molecule with lowest Gibbs free energy has been selected from isomers (Kaltsoyannis and Plane, 2008; Khanniche et al., 2016; Kim and Yoo, 2016) , and details of the structures and coordinates are provided in SI (Figure S1 and Table S3).”

To ensure clarity for the readers, in the revised SI, we have presented the considered isomers together with their calculated Gibbs free energies in Fig. S1, and the corresponding coordinates are summarized in Table S3.

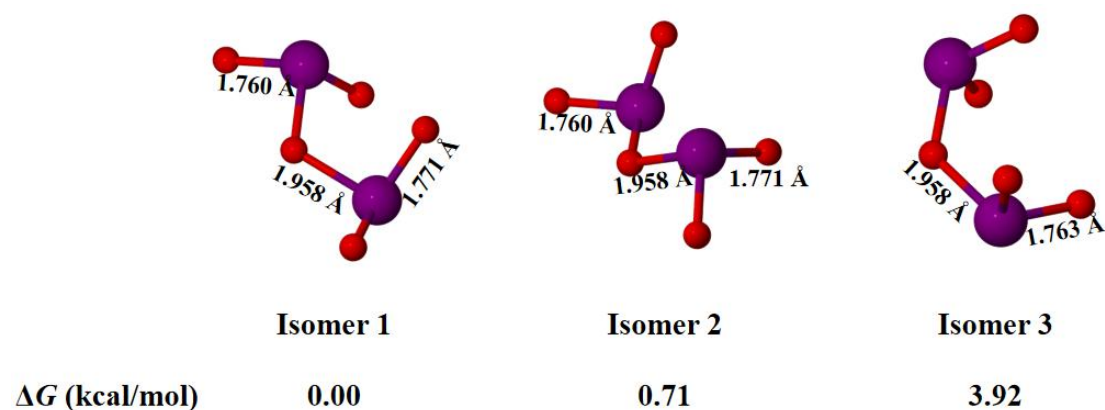


Figure S1. The optimized structures for isomers of I₂O₅ at the M06-2X/aug-cc-pVTZ(-PP) level of theory. The relative Gibbs free energies (kcal/mol, comparing to isomer 1) are provided beneath the corresponding isomers.

Table S3. Coordinates for all calculated isomers of I₂O₅ at the M06-2X/aug-cc-pVTZ(-PP) level of theory.

Isomer 1			
O	-0.000013	-0.988788	0.000159
I	1.641204	0.055287	-0.225857
I	-1.641235	0.055311	0.225852
O	2.800249	-1.108887	0.404898
O	1.270721	1.236952	1.040258
O	-2.800236	-1.108859	-0.404989
O	-1.270515	1.236874	-1.040296
Isomer 2			
I	0.000000	1.656872	-0.054736
O	0.000000	0.000000	0.989073
I	0.000000	-1.656872	-0.054736
O	-0.789433	-2.716528	1.107431
O	1.199506	1.113881	-1.239338
O	0.789433	2.716528	1.107431
O	-1.199506	-1.113881	-1.239338
Isomer 3			
I	-1.769146	-0.160199	-0.157389
O	-0.000002	0.000007	-0.980462
I	1.769147	0.160192	-0.157396
O	-2.140622	1.528856	0.182916
O	-1.400607	-0.996020	1.350040
O	1.400657	0.996070	1.350017

O	2.140569	-1.528872	0.182940
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Across the heterogeneous hydrolysis pathways of I_2O_5 presented in this study, whether mediated by water, iodic acid, I_2O_5 , or pollutants, the cleavage always occurs at the central I–O covalent bond of the I_2O_5 . This appears to be a consequence of the CV definition, which biases the system toward iodic acid formation. Nevertheless, the rationale for this setup should be substantiated by chemical evidence. A wavefunction analysis, such as bond order calculations, could be provided to confirm that the central I–O bond is indeed the weak, thereby justifying its designation as the most likely bond to break.

Response: According to the reviewer’s suggestion, we have calculated the Mayer bond order (MBO) of adopted I_2O_5 molecule by Multiwfn 3.7 (Lu and Chen, 2012). As shown in Figure S3, the central I–O bond is considered to be a single bond (MBO: 0.864), while the terminal I–O bond is thought to be a double bond (MBO: 1.729). The results indicate that initial cleavage is expected to occur at the central but weaker I–O covalent bond of the I_2O_5 . We have supplemented the chemical-bond characterization for this part in the SI as the reviewer suggested. This result provides compelling chemical evidence supporting the rationality of the CV settings.

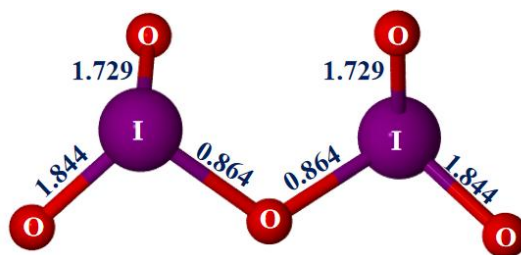


Figure S3. Mayer bond orders for I_2O_5 calculated at the M06-2X/cc-pVTZ(-PP) level of theory.

Atmospheric iodine species and pollutants are more diverse than the limited set examined here. For example, even in the case of amines, more than one hundred species exist in the atmosphere. It would be helpful if the authors could include a brief discussion of the possible roles of other atmospheric components, or at minimum acknowledge this as a limitation of the current study.

Response: Thank you for this insightful suggestion. This helps readers understand the limitations of the study. The real atmosphere is complex; as the reviewer noted, iodine species (e.g. HOI, HIO₂, HIO₃, I₂O₃, I₂O₄, and I₂O₅) and atmospheric pollutants (e.g. H₂SO₄, HNO₃, dimethyl sulfide, organic acids, and aromatic hydrocarbons)-including amines-are highly diverse. We consider that other components are also likely to influence the heterogeneous hydrolysis process of the I₂O₅ of interest. In this study, the effects of I₂O₅ and HIO₃ on the reaction are explored here mainly because, as reactants and products, they are most likely to coexist in the same environment, thereby facilitating self catalysis. Meanwhile, we chose H₂SO₄ and amines (i.e. MA, DMA, and TMA) as the representative acid and base pollutants that are associated with aerosol particle formation. We have expanded this part of the discussion to better reflect real atmospheric conditions and acknowledge the limitation that the manuscript can not comprehensively examine all species in revised manuscript as follows (Page 12, line 304):

“The real atmosphere is chemically complex, including iodine species (e.g. HOI, HIO₂, HIO₃, I₂O₃, I₂O₄, and I₂O₅) and atmospheric pollutants (e.g. H₂SO₄, HNO₃, organic acids, and ammonia), which are likely to influence the heterogeneous hydrolysis of I₂O₅. In future work, we intend to confirm the impacts from other atmospheric components.”

Minor Comments:

Page 5, Line 139: “...along the Z axis...” Units are missing.

Page 6, Line 165: “Pink, red, white atoms represent I, O, H in sequence (The same below).”

This sentence should be: “The pink, red, and white spheres represent I, O, and H atoms, respectively (the same applies in Figures 3–6 below).”

Lines 203 and 226: ‘Profiles’ should be ‘The profile’

Lines 188: ‘error bands’ should be ‘error band’

Line 240: It is recommended to remove this citation, as it does not appear to provide effective support.

Response: We appreciate the reviewer’s careful evaluation. Accordingly, we have completed all corresponding revisions in response to the reviewer’s minor comments.

Reference:

- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16 Rev. A.01; Gaussian, Inc.: Wallingford, CT, 2016.
- Kaltsoyannis, N. and Plane, J. M. C.: Quantum chemical calculations on a selection of iodine-containing species (IO, OIO, INO₃, (IO)₂, I₂O₃, I₂O₄ and I₂O₅) of importance in the atmosphere, *Phys. Chem. Chem. Phys.*, 10, 1723, <https://doi.org/10.1039/b715687c>, 2008.
- Khanniche, S., Louis, F., Cantrel, L., and Černušák, I.: Computational study of the I₂O₅+H₂O = 2 HOIO₂ gas-phase reaction, *Chem. Phys. Lett.*, 662, 114–119, <https://doi.org/10.1016/j.cplett.2016.09.023>, 2016.
- Kim, M. and Yoo, C.-S.: Phase transitions in I₂O₅ at high pressures: Raman and X-ray diffraction studies, *Chem. Phys. Lett.*, 648, 13–18, <https://doi.org/10.1016/j.cplett.2016.01.043>, 2016.
- Lu, T. and Chen, F.: Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.*, 33, 580–592, <https://doi.org/10.1002/jcc.22885>, 2012.