Response to the community #1 Comments for the manuscript "Reaction between perfluoroaldehydes and hydroperoxy radical in the atmosphere: Reaction mechanisms, reaction kinetics modelling, and atmospheric implications**"**

Comment: Line 95: In addition, multi-structural torsional anharmonicity involving reactant and transition state were all calculated using MS-T method (multi-structural method for torsional anharmonicity. How was this done? Can you please elaborate.

Response:

(a)Theoretical background

The complete conformational-rotational-vibrational partition functions involving reactant and transition state have been all calculated by using MS-T method (multistructural method for torsional anharmonicity)(Zheng and Truhlar, 2013) and executed through MSTor program package.(Chen et al., 2023) In general, the conformational-rotational-vibrational partition function is calculated as,

$$Q_{con-rovib}^{MS-T,X} = \sum_{j=1}^{J} Q_{rot,j}\, exp(-\beta U_j)\, Q_j^{HO}\, Z_j \prod_{t=1}^{t} f_{j,\tau} \qquad (1)$$

where "con" and "rovib" denote conformation and rotation-vibration, respectively, J is the number of distinguishable conformational structures (j = 1, 2, ⋯, J). β = 1/k_bT and X labels reactants, products or transition states. $Q_{rot,j}$, U_j and Q_j^{HO} represent the classical rotational partition of structure j, energy gap relative to the global minimum energy structure, and the normal-mode harmonic oscillator vibration partition function of the J^{th} structure, respectively. Z_j is a factor to ensure that the MS-T scheme reaches the correct high-Temperatre limit (within the parameter range of the model), and $f_{j,\tau}$ is an internal coordinate torsional nonharmonic function that adjusts the harmonic partition function of structure j to account for torsional motion τ.

When equation (1) is used for a single-structure (SS) rotation-vibrational partition function of the conformer j (generally, the global minima structure (j = 1)), and if Z_j and $f_{j,\tau}$ were set to 1, the partition function $Q_{con-rovib}^{MS-T,X}$ reduces to the multi-structural local-harmonic (MS-LH) partition function. Thus,we can rewrite it as

$$Q_{rovib,j}^{SS-HO} = Q_{rot,j}\, exp(-\beta U_j)\, Q_{vib,j}^{HO} \qquad (2)$$

Subsequently, the multistructural torsional anharmonicity factor $F^{MS-T,X}$ will be defined for reactants and transition states by using equation (1) and (2) as shown below

$$F^{MS-T,X} = Q_{con-rovib}^{MS-T,X} / Q_{rovib,1}^{SS-HO} \qquad (3)$$

also, the corresponding multistructural torsional anharmonicity factor for the reaction

$$F^{MS-T,X} = Q_{sp}^{MS-T} / Q_R^{MS-T} \qquad (4)$$

The reaction rate constant for biomolecular was calculated as

$$k^{MS-T} = \kappa\sigma \frac{k_B T}{h} \frac{Q_{elec}^{\neq} Q_{con-rovib}^{MS-T,\neq}}{N_a Q_{elec}^{R} Q_{con-rovib}^{MS-T,R}} exp(-\beta V^{\neq}) \qquad (5)$$

where k_b is Boltzmann's constant, T is the temperature, N is Avogadro's number, h is Planck's constant, and β is $1/k_b$T. $V^{\neq}$ denotes the classic reaction energy barrier exclude ZPE correction. Q_{elec} represent electronic partition function, while κ and σ denote Eckart tunneling coefficient and the reaction symmetry number, respectively.

(b) Calculated details

(1) Conformational Search: Use **ConfGen.exe** to generate initial structures by rotating specified bonds

(2) Geometry Optimization & Frequency Calculation: Optimize structures using Gaussian and remove duplicates (e.g., mirrored/rotationally equivalent structures). Run frequency calculations to obtain Hessians and energies.

(3) Distinct Structure Identification: Use **mvinput.exe** to exclude mirror images and rotationally redundant structures. Generate *mvorm.inp* for Voronoi tessellation

(4) Torsional Periodicity ($M_{j,\tau}$): Compute $M_{j,\tau}$ values using **mcvorm.exe** (Monte Carlo) or vorm.exe (Voronoi tessellation).

(5) Input File Generation: Combine Gaussian .fchk files into *all.fchk*. Use **msinput.exe** to generate *mstor.inp* and *hess.dat*, adding uncoupled torsions.

(6) Execution: Run mstor.exe with the MS-T(CD) method to calculate partition functions and thermodynamic properties.

(c) Input files for the ConfGen.exe executable

```
13 2
C              1.01911500   -0.47626600    0.05443400
```

```
 C              2.35234900    0.19807600    0.44862800
 H              2.51946100    0.29297300    1.53563000
 C             -0.15660500    0.51749400    0.11794900
 O              3.12769000    0.56284200   -0.38553200
 F              0.04052700    1.46045400   -0.81804700
 F             -0.13406100    1.10278400    1.33631400
 F              1.10175100   -0.98403000   -1.18192700
 F              0.78274500   -1.47995300    0.93436300
 C             -1.56560300   -0.07991200   -0.09014200
 F             -2.45510800    0.91017100   -0.11075900
 F             -1.62361100   -0.73826800   -1.24442900
 F             -1.87185600   -0.91027500    0.90264400
#torsion 1 definition
 2 1
 3
 5 2 3
 3
 0.0 120.0 -120.0
#torsion 2 definition
 1 4
 6
 1 8 9 2 3 5
 3
 0.0 120.0 -120.0
%nprocshared=12
%mem=80GB
# M062x/gen opt=calcfc int=grid=99974 scf=conver=11
 0 1
@/home/zgdong/mg3s.gbs
Extbasis
```

Reference

Chen, W., Zheng, J., Bao, J. L., Truhlar, D. G., and Xu, X.: MSTor 2023: A new version of the computer code for multistructural torsional anharmonicity, now with automatic torsional identification using redundant internal coordinates, Computer Physics Communications, 288, 108740, https://doi.org/10.1016/j.cpc.2023.108740, 2023.

Zheng, J. and Truhlar, D. G.: Quantum thermochemistry: Multistructural method with torsional anharmonicity based on a coupled torsional potential, Journal of Chemical Theory and Computation, 9, 1356–1367, https://doi.org/10.1021/ct3010722, 2013.