

## Model

A vibrationally-resolved master equation using only QCT-computed rates is utilized for TC1A.1 and TC1A.2. Trans-rotational equilibrium is assumed.  $O_3$  transitions were computed on the nine PESs of Varga et al.,<sup>1</sup>  $O_4$  transitions were computed on the triplet PES of Paukku et al.,<sup>2</sup>  $N_3$  transitions were taken from the NASA Ames database,<sup>3,4</sup> and  $N_4$  transitions were computed on the PES of Paukku et al.<sup>5</sup> Double dissociation events and vibration-vibration energy transfer are neglected.

For computational efficiency, diatom-diatom transitions were calculated assuming all collisions occur with a molecule in the ground vibrational state. This assumption is based on the idea that a molecule in the ground state is the most probable collision partner and that the projectile molecule's internal energy is not as influential in determining the outcome of a collision event as the target molecule's internal energy. Since projectile molecule vibrational states do not change (vibration-vibration energy exchange is not considered, and only the ground vibrational level is used as the projectile's initial state), final rate coefficients for all transitions are of the form  $K_{v \rightarrow v'}$ , where  $v$  and  $v'$  are the initial and final vibrational state respectively.

## References

<sup>1</sup>Z. Varga, Y. Paukku, and D. G. Truhlar, "Potential energy surfaces for  $O+O_2$  collisions," *The Journal of chemical physics*, vol. 147, no. 15, p. 154312, 2017.

<sup>2</sup>Y. Paukku, Z. Varga, and D. G. Truhlar, "Potential energy surface of triplet  $O_4$ ," *The Journal of chemical physics*, vol. 148, no. 12, p. 124314, 2018.

<sup>3</sup>R. Jaffe, D. Schwenke, G. Chaban, and W. Huo, "Vibrational and rotational excitation and relaxation of nitrogen from accurate theoretical calculations," in *46th AIAA Aerospace Sciences Meeting and Exhibit*, p. 1208, 2008.

<sup>4</sup>G. Chaban, R. Jaffe, D. Schwenke, and W. Huo, "Dissociation cross sections and rate coefficients for nitrogen from accurate theoretical calculations," in *46th AIAA Aerospace Sciences Meeting and Exhibit*, p. 1209, 2008.

<sup>5</sup>J. D. Bender, P. Valentini, I. Nompelis, Y. Paukku, Z. Varga, D. G. Truhlar, T. Schwartzentruber, and G. V. Candler, "An improved potential energy surface and multi-temperature quasiclassical trajectory calculations of  $N_2+N_2$  dissociation reactions," *The Journal of chemical physics*, vol. 143, no. 5, p. 054304, 2015.