New insights on the ozone formation reaction

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Introduction

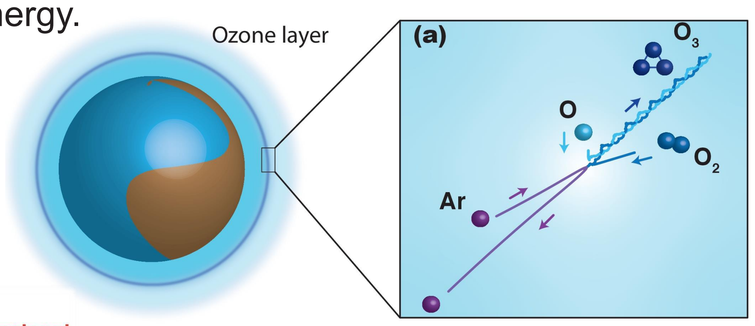
Absorbing UV radiation, ozone (O_3) that exists in the stratosphere protects life on Earth and plays a crucial role in Earth's temperature balance. In contrast, tropospheric ozone is considered an important greenhouse gas and air pollutant. However, despite its importance and decades of research, the reaction leading to ozone formation is not fully understood due to its complexity.

Method

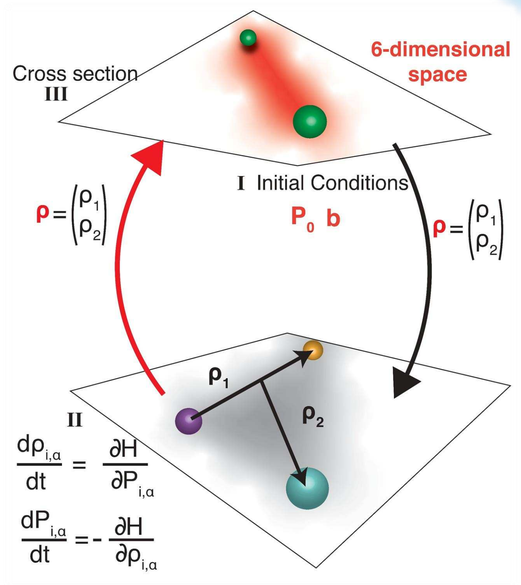
Direct ternary recombination reaction is a three-body collision that in which two of the reactants form a bound state and the third one carries away part of the binding energy.

$$A + A + A \rightarrow A_2 + A$$

Full quantum scattering calculations for the system are practically unfeasible.



$$O_2 + O + Ar \rightarrow O_3 + Ar$$



A Classical trajectory method in hyperspherical coordinates (from [2]) is adapted to this problem representing the O_2 molecule as a super-atom. Thus resulting in a fixed angle between O_2 and the direction to O, corresponding to the bond angle in O_3(117°).

Interactions

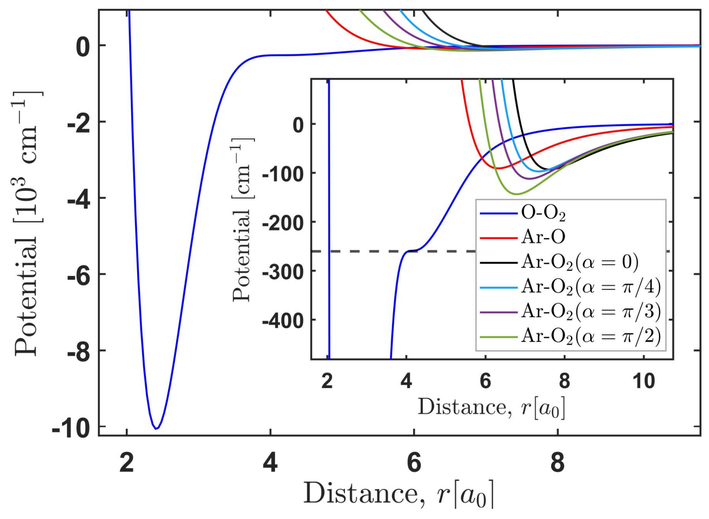
The ArO_3 potential is assumed as the sum:

$$V = V_{O-O_2} + V_{Ar-O_2} + V_{Ar-O}$$

Potential energy surfaces are *ab initio* potentials. V_{Ar-O_2} and V_{Ar-O} are constructed using UCCSD(T)-F12a method with the aug-cc-pVTZ basis set. V_{O-O_2} is constructed in [3].

The interaction of Ar with O_3 does not depend significantly on the angle between the plane of $O + O_2$ and the direction to Ar, so to simplify the numerical calculations this angle is set to zero.

The angle α between O_2 and Ar is considered a parameter of the problem and the results are averaged over this parameter.



Result

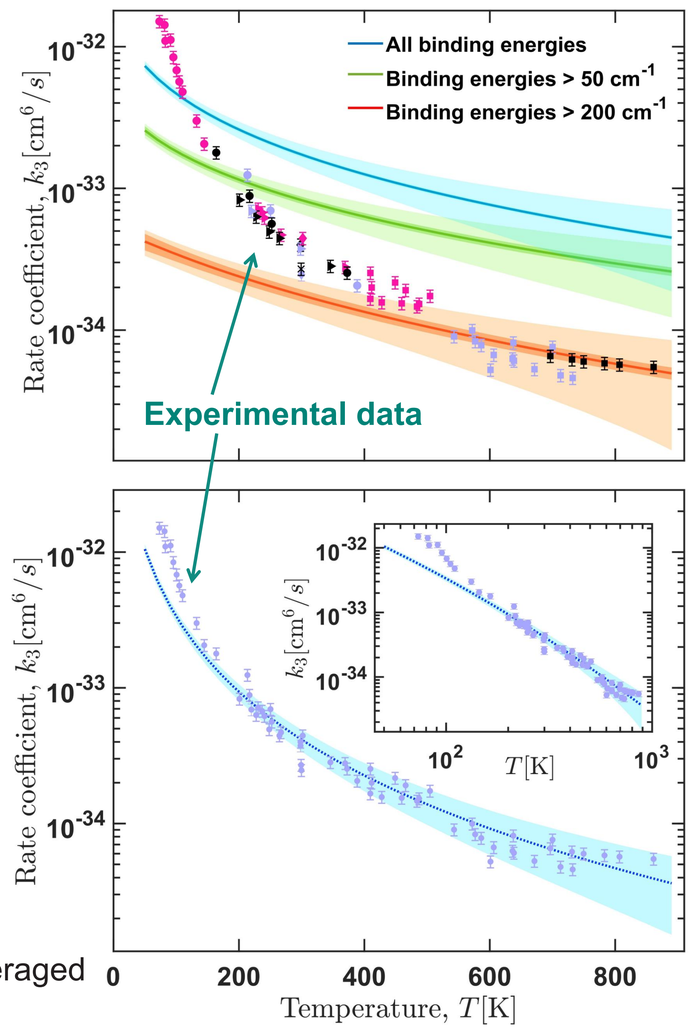
Comparison of the analytic rate coefficients with the available experimental data:

In an experiment at a given temperature T, only those molecules with binding energies $> T$ are collisionally stabilized and accounted for.

Vibrational quenching is the vibrational de-excitation of the highly excited O_3 molecules in collisions with other species. To account for this process we should scale the results by factor of (in units of Kelvin)

$$\Delta E/T = 70/T$$

ΔE : energy of $Ar - O_3$ interaction averaged over involved vibrational states of O_3.



Two-step mechanisms in ozone formation:
The stabilization (or energy-transfer) mechanism: formation of long-lived rovibrational resonance O_3^* as intermediate complex,

$$O_2 + O \rightarrow O_3^*$$
$$O_3^* \rightarrow O_2 + O$$
$$O_3^* + Ar \rightarrow O_3 + Ar$$

The Chaperon mechanism: formation of a temporary complex O_2Ar^* or OAr^*,

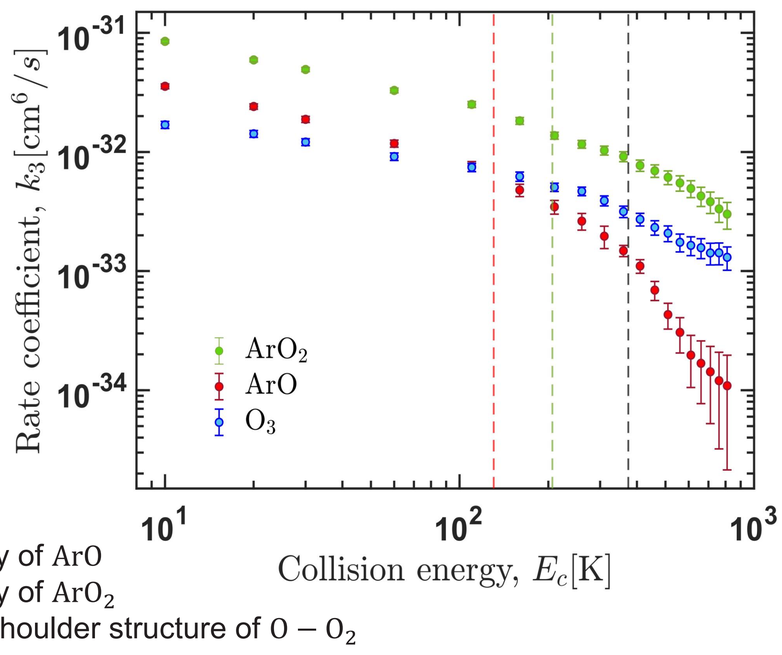
$$O_2 + Ar \rightarrow O_2Ar^*$$
$$O_2Ar^* \rightarrow O_2 + Ar$$
$$O_2Ar^* + O \rightarrow O_3 + Ar$$

or

$$O + Ar \rightarrow OAr^*$$
$$OAr^* \rightarrow O + Ar$$
$$OAr^* + O_2 \rightarrow O_3 + Ar$$

A reliable measure to analyse the importance of one of the two-step mechanisms is the direct three-body recombination rate coefficient: The Chaperon mechanism is dominant at $E_c < 200$K, while the stabilization mechanism appears to be dominant at $E_c > 700$K.

Changes in the power-law behaviour around dissociation energies and shoulder structure.



Conclusion

- It is found that the majority of O_3 molecules formed initially are weakly bound, and thus, destroyed in collisions with other species.
- The rate coefficients for the direct formation of O_3 in ternary collisions $O_2 + O + Ar$ derived for temperatures 50-900 K shows a good agreement with available experimental data for temperatures 100-900 K after considering the effect of the vibrational quenching process.
- At temperatures 50-100 K theory gives smaller rate coefficients. It is likely that the classical approach is not applicable for these temperatures.
- The formation of ozone in ternary collisions $O_2 + O + Ar$ at temperatures 200 K-700 K, cannot be viewed as a two-step mechanism.

Reference

[1] M. Mirahmadi, J. Pérez-Ríos et al., *Phys. Rev. Lett.* **2022**, 128, 108501.
[2] J. Pérez-Ríos, *An Introduction to Cold and Ultracold Chemistry*, Springer Int. Pub. **2020**.
[3] V. G. Tyuterev et al., *J. Chem. Phys.* **2013**, 139, 134307.