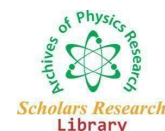




Extended Abstract

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The O + O₂ exchange reaction: symmetry, isotope effects, and influence of molecular forces

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Statement of the Problem: Molecular oxygen O₂ is the most important molecule in Earth's atmosphere and stratospheric ozone O₃ protects us from 97% of UV radiations. The abundance in ¹⁶O being 99.8%, O₂ and O₃ exclusively formed from it are dominant, thereby giving a reference for any process involving oxygen. A strong enrichment (about 10%) of O₃ in both ¹⁸O and ¹⁷O (the so-called mass-independent fractionation MIF), has first been observed decades ago. The three body recombination O + O₂ + M → O₃ + M is believed to be the main process leading to this enrichment and at low pressures, it can be partitioned into two steps: the formation of O₃ in a highly excited rovibrational state, from reaction O + O₂ → O₃^{*}, and its subsequent stabilization by collision with an energy absorbing partner M (say N₂ or O₂), O₃^{*} + M → O₃ + M. Thus, the efficiency of the exchange reaction O + O₂ → O₃^{*} → O₂ + O, involving metastable O₃^{*} as an intermediate, is one of the key parameters to understand ozone formation. This reaction is very fast and competes with the stabilization process. The reaction of O atoms with O₂ molecules has been widely studied both experimentally and theoretically. The importance of the reaction lies in the fact that this is the way of stratospheric ozone formation: ozone can be stabilized when the initially formed O₃ collision complex lives long enough to be hit by a collision partner that reduces its internal energy so that it cannot dissociate. Another reason for the interest in the reaction is the so-called mass-independent isotope effect, which leads to anomalous isotope abundance of oxygen in stratospheric ozone. Collisional energy transfer plays an essential role in ozone formation, and the fate of the collision complex depends on the lifetime and the internal dynamics of the complex, which may be isotope-dependent. The question of the origin of the mass independence of enrichment of isotopes ¹⁷O and ¹⁸O has not been answered yet and is the subject of recent experimental and theoretical activity. The standard method of the theoretical description of unimolecular and recombination reactions, RRKM theory, is based on a statistical assumption and proved not to be able to explain the experimentally observed isotope enrichment ratios unless an ad hoc factor related to the effective density of states of symmetric vs asymmetric ozone is introduced. The reasons for the need for such a factor are not yet understood, but it does reflect the important role of internal dynamics. Theoretical work has demonstrated that the O + O₂ atom exchange reaction indeed displays nonstatistical behavior, independently of its isotope constitution.

The actual dynamics in O + O₂ collisions can be studied in most detail in direct dynamical experiments, namely, measurements using crossed molecular beams. In this kind of experiment, isotope labeling is necessarily used because this is the only way to identify the products of collision. Labeling allows quantitative studies of reactive and inelastic events in the same experimental setup. Cross section measurements utilizing labeling have been performed at collision energies of 5.7 and 7.3 kcal mol⁻¹ using the ¹⁸O + ³²O₂ mass combination.

Methodology: Using a newly developed, very accurate, potential energy surface (PES), we have realized computationally intensive full-quantum investigation of the dynamics of this process, using a time-independent formalism. QCT calculations have been performed according to the standard methodology, with the specific features described in refs. Similar to refs, we used the PES developed by Babikov et al. for the electronic ground state. Test calculations have been performed on the PES of Dawes et al., and we found that at the high collision energies dominating our study the results are not sensitive to the presence or absence of the reef appearing on the Babikov PES. At the very high collision energies, the available energy exceeds that necessary for electronic excitation, and nonadiabatic transitions could be possible. However, in the theory–experiment comparison in, the QCT calculations confined to the ground state reproduced the experimental results well without considering any nonadiabatic effect. From this, we surmised that the latter are probably not important in reaction 1 even at very large collision energies.

Results: We have, from first principles, computed reactive cross sections and reproduced measured rate constant for the ¹⁸O + ³²O₂ process, within experimental error bars. We will sum up resulting cross sections and rate constants for the various ¹⁶O + ³²O₂, ¹⁸O + ³²O₂, ¹⁷O + ³²O₂, ¹⁶O + ³⁶O₂ and ¹⁶O + ³⁴O₂ processes, discussing isotope effects and inclusion of permutation symmetry. We will discuss the strong influence of the PES.

Bottom Note: This work is partly presented at *5th International Conference on Physical and Theoretical Chemistry* October 11-13, 2018, Edinburgh, Scotland