

Intitulé français du sujet de thèse proposé:

Etude de dynamique quantique de collisions avec l'ozone comme complexe intermédiaire

Intitulé en anglais:

Quantum dynamical study of collisions involving ozone as intermediate

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Domaine scientifique principal de la thèse: Molecular physics

Domaine scientifique secondaire de la thèse: Quantum reactive scattering

Financement envisagé (Ministère, Région, , ...): Ministère

Description du projet scientifique :

Ozone is one of the most extensively studied small polyatomic molecules due to its fundamental importance in atmospheric chemistry. Despite enormous efforts, our understanding of this molecular system is still far from complete. The stratospheric ozone O_3 molecule with three ^{16}O atoms is most abundant in the atmosphere. However, a strong enrichment of about 10%, with respect to what happens for O_2 , in ^{17}O and ^{18}O has been found in ozone more than thirty years ago [1]. It is almost similar for both ^{17}O and ^{18}O and known as the so-called mass-independent fractionation (MIF) in the formation of ozone. It has also been observed in laboratory experiments [2].

The $O + O_2$ collision, which is the subject of this thesis, is now known to play a key role in the formation of atmospheric ozone, because it is intimately related to the ozone formation recombination reaction, $O + O_2 + M \rightarrow O_3 + M$. Indeed they proceed through the same ro-vibrationally excited intermediate complex, O_3^* . M is a buffer bath gas atom or molecule, most likely nitrogen N_2 , that stabilizes this metastable complex. An in-depth understanding of bimolecular isotope exchange reactions [3] will therefore not only advance our knowledge of complex-forming reactions in general, but also shed light on the MIF in the formation of ozone, which is an unresolved puzzle till date. It is now experimentally well established that MIF is due to a significant isotopic effect observed in the ozone formation reaction. The latter originates from the difference in the lifetimes of the intermediate complexes, O_3^* , and in the zero-point vibrational energy difference of O_2 fragments to which the intermediate can dissociate.

The purpose of the thesis is to study the $O + O_2$ isotopic variants and especially to provide the

most rigorous and complete description of the lifetime spectrum of O_3^* involved in the $O + O_2$ collisions occurring in the Earth's atmosphere, including all associated isotope effects. The aim is therefore to correctly describe the quantum resonances associated to the O_3^* complex formed in the deep well of the interaction potential, and thus to obtain accurate lifetime of the metastable O_3^* states of ozone, owing to their important role in the understanding of the MIF. The calculation of the lifetimes and energies of the O_3^* intermediate complex will be performed using a sophisticated treatment. Two complementary accurate quantum mechanical methods will be used to treat the collisional dynamics: a Time Independent Quantum Mechanical method in hyperspherical coordinates and a Time Dependent Wave Packet method in Jacobi coordinates. The most recent high quality ab initio interaction potentials for O_3 will be employed for the purpose. To our knowledge, this will be the first detailed quantum mechanical study of the O_3^* lifetimes including the permutation symmetry of the O_2 and O_3 systems.

References

1. K. Mauersberger, *Ozone Isotope Measurement in the Stratosphere*, Geophys. Res. Lett. 14, 80 (1987).
2. M. H. Thiemens and J. E. Heidenreich III, *The Mass-Independent Fractionation of Oxygen: A Novel Isotope Effect and Its Possible Cosmochemical Implications*, Science 219, 1073 (1983).
3. T.R. Rao, G. Guillon, S. Mahapatra, P. Honvault, *Huge Quantum Symmetry Effect in the $O + O_2$ Exchange Reaction*, J. Phys. Chem. Lett. 6, 633 (2015).

Connaissances et compétences requises: Quantum physics, Molecular physics