Joint CQSE and CASTS Seminar

Weekly Seminar
Mar. 18, 2016 (Friday)

TIME Mar. 18, 2016, 14:30 ~ 15:30
TITLE Decomposition of carbonyl oxide: Importance of quantum tunneling and internal rotation
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Abstract

Atmospherically relevant carbonyl oxide R_1R_2COO, so-called Criegee intermediates (CI's), can have many different forms depending on the substituents R_1 and R_2. These strong oxidizing species are the key intermediate in the ozonolysis of different kinds of alkenes in the atmosphere. Due to CI's active participation in atmospheric chemistry, such as oxidation, aerosol formation and OH radical production, the atmospheric fate of this very reactive species is a very important topic. However, presently there are no effective methods to measure the CI concentration in the atmosphere. Thus the only way to know the CI concentration is through the rate of its production and removal. However, the accurate rates for removal even the simplest CH_2OO was not measured experimentally until very recently. Considering the abundance of water in the atmosphere, the reaction rate of CI's and water vapor is a very important quantity to accurately model the removal rate of CI. In addition, experimental studies have shown that CI may self-decompose at atmospherically relevant pressure and temperature. With experimental difficulties to observe the rate for larger species, we turn to theoretical simulations.

We considered the reaction of CI + H_2O and CI + $(H_2O)_2$, to model the process of water vapor reaction. We will report theoretical results for simplest H_2COO, methyl CH_3CHOO, dimethyl $(CH_3)_2COO$, and ethyl CH_3CH_2CHOO CI's. Furthermore, for the self-decomposition, we found that there are two channels that become relevant depending on the substituent position. To obtain accurate rate coefficients, we paid detailed attention toward the floppy modes that are important for water dimer. Furthermore, we show that although the water reaction and one of the self-decomposition reaction proceeds with Hydrogen atom transfer, tunneling effect is only significant for the latter. From our computational results we clarify the effect of conformation, and the effect of chain length toward reactivity. Furthermore, detailed

analysis is performed to understand the curious temperature dependence seen for the CI water vapor reaction.