P-08

Poster Session Day 1

An RRKM and experiment-based model of isotopic fractionation in formaldehyde photolysis

Luisa Pennacchio[1], *Zacharias Liasi*[1], *Thomas Röckmann*[2], *Kurt V. Mikkelsen*[1], *& Matthew S. Johnson*[1]

[1] Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
[2] Institute for Marine and Atmospheric Research Utrecht (IMAU), Utrecht University, Utrecht, The Netherlands
*Presenting Author Email: lupe@chem.ku.dk

Formaldehyde is a short-lived intermediate formed by the oxidation of virtually every VOC in the atmosphere. It is the source of half of atmospheric hydrogen, and a large source of CO and CO_2, and plays a role in particle growth. Efforts to better understand the remarkable transformations of formaldehyde are hindered due to lack of knowledge of some of the basic processes in formaldehyde photolysis. Here, we present a combined Rice–Ramsperger–Kassel–Marcus (RRKM) and experiment-based model that significantly advances our ability to describe photolytic kinetic isotope effects and their pressure dependencies. RRKM theory was used to calculate the decomposition rates of the S0, S1 and T1 states using CCSD(T)/aug-cc-pVTZ, ωB97X-D/aug-cc-pVTZ and CASPT2/aug-cc-pVTZ levels of theory. Experimental internal conversion and intersystem crossing rates were used and modified with the density of states of the isotopologues based on Fermi's 'Golden Rule'. The following isotopologues of formaldehyde were investigated: HCHO, DCHO, DCDO, $D^{13}CHO$, $H^{13}CHO$, $HCH^{17}O$, $HCH^{18}O$, $H^{13}CH^{17}O$ and $H^{13}CH^{18}O$. The method and mechanism were validated by comparison to all existing and newly obtained experimental data. The model was able to accurately replicate the experimental pressure trends of the kinetic isotope effects (KIEs) and was in excellent agreement. The large isotope effects of heavy carbon and oxygen were found to be primarily due to non-RRKM behavior. The model was used to predict the KIEs and the molecular hydrogen yields of the deuterated species at varying altitudes.