



Tuesday, November 29, 2016

3:30pm-4:30pm (refreshments at 3:15pm)

Bechtel Collaboratory in the Discovery Learning Center (DLC)

University of Colorado, Boulder

“Minor” Molecular Thermochemistry Effects Significantly Alter Predictions of Global Combustion Phenomena

Nicole Labbe, *University of Colorado, Boulder*

CH_3 , the simplest alkyl radical, is an extremely stable intermediate with a C-H bond energy of $D_0(\text{H}-\text{CH}_2) = 109.28 \pm 0.03$ kcal/mol, according to Active Thermochemical Tables (ATcT). Consequently, it persists in large concentrations even in high temperature chemically reacting systems such as flames. The dominant process for CH_3 removal in combustion and flame processes is through radical-radical recombination, either with H-atoms (R1: $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$; $\Delta H_{0\text{K}} = -103.34 \pm 0.02$ kcal/mol, ATcT) or with itself (R2: $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$; $\Delta H_{0\text{K}} = -87.92 \pm 0.05$ kcal/mol, ATcT). For reaction (R1), direct measurements for k_1 are largely limited to low temperatures, while direct shock tube measurements for k_{-1} span a temperature range from 1700 to 4500 K. Reconciling the apparently disparate experimental databases on k_1 and k_{-1} requires accurate equilibrium constants for reaction (R1) spanning an extended range of temperatures (300-4500K). While several thermochemical databases have accounted for anharmonic effects in calculations of CH_4 thermochemistry, analogous corrections have not been included in CH_3 radical thermochemistry. As a consequence, existing literature assessments of the equilibrium and rate constants for recombination/dissociation reaction (R1) have notable inaccuracies.

In the present work, we include all relevant anharmonic corrections to calculate an accurate ATcT partition function for CH_3 . The resulting nonrigid-rotator-anharmonic-oscillator partition function is used to determine thermochemical parameters over a wide temperature range (200-6000 K) of relevance to atmospheric and combustion chemistry. The new ATcT thermochemistry is also used to prescribe K_{eq} values for reaction R1. Furthermore, literature experiments and theory (based on two-dimensional master equation calculations with a first principles energy and angular momentum transfer kernel) are used to obtain an accurate representation of the kinetics for $k_{1,-1}(T,P)$ for subsequent use in combustion modeling. Theory is also used to predict the effects of bath-gas colliders on $k_{1,-1}(T,P)$. Lastly, we assess the impact of incorporating anharmonic thermochemistry for CH_3 and the updated fits for $k_{1,-1}$ in current widely used literature models for simulations of CH_4 -air laminar flame speeds.

Biography: Nicole J. Labbe is an Assistant Professor of Mechanical Engineering at the University of Colorado Boulder. She received her Ph.D. in Chemical Engineering from the University of Massachusetts Amherst in 2013. Before joining the faculty at the University of Colorado in 2016, Professor Labbe was a postdoctoral associate in the Chemical Sciences and Engineering division of Argonne National Laboratory. Professor Labbe's research focuses on several areas of gas phase chemical kinetics, especially in the areas of theoretical chemistry and reaction rate theory, kinetic modeling and combustion dynamics, and renewable liquid fuel design. Her Ph.D. research focused on understanding the energetic and environmental implications of including heteroatoms (fuel-bound nitrogen and oxygen atoms) for biofuels and hypergolic rocket propellants. Her postdoctoral research involved using theoretical chemistry to study common combustion radical kinetics and understand how their dynamics affect predictions of global combustion phenomena.

