

Probing Entrance and Exit Channel Dynamics in Hydroxyl Radical Reactions by Photodetachment

Content

Studies using the photodetachment of precursor negative ions to examine the transition state dynamics of hydroxyl radical reactions will be reviewed. In cases where the anion has a geometry similar to the transition-state region for a bimolecular neutral reaction, dissociative photodetachment occurs, and a photoelectron-photofragment coincidence experiment can be used to kinematically characterize the resulting dissociation event, allowing a correlation of the electron kinetic energy distribution determined by Franck-Condon photodetachment with the final neutral product states determined by the kinetic energy release between the neutral atomic and molecular products. Examples will include a benchmark measurement of the dynamics of an elementary chemical reaction: using the $F^-(H_2O)$ complex to study the $F + H_2O \rightarrow OH + HF$ neutral reaction. This four-atom system has six internal degrees of freedom and represents a grand-challenge for accurate calculations of the Born-Oppenheimer potential energy surfaces and quantum dynamics of the system. Comparison of experiment with theoretical predictions shows that this system can be treated with near chemical accuracy, but there are still challenges in accounting for excited states and long-lived complexes.¹ Extension of this method to examining the effect of parent anion vibrational excitation on the dissociation dynamics on the neutral surface through overtone excitation of the F-H-O proton transfer coordinate in the anion will also be discussed,² as well as the prospects for further studies of the effects of vibrational excitation. This work has been supported in part by the US DOE under grant DE-FG03-98ER14879

References

- [1] R. Otto, J. Ma, A.W. Ray, J.S. Daluz, J. Li, H. Guo and R.E. Continetti, *Science* 343, 396 (2014)
- [2] A.W. Ray, J. Ma, R. Otto, J. Li, H. Guo and R.E. Continetti, *Chemical Science* 8, 7821 (2017)

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