Spectroscopy of organic atmospheric chromophores at or near the water-air interface

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Spectroscopy is a powerful tool in the study of photoreaction dynamics. Fundamental reaction dynamics of sunlight initiated processing of organic molecules in aqueous environments characteristic of planetary atmospheres including the contemporary and prebiotic Earth are described in this presentation.

Atmospheric photochemistry traditionally involves excitation in the ultraviolet where the energy of solar photons exceeds the bond dissociation energy of trace atmospheric species. Our work extended traditional photochemical studies to ground electronic state chemistry occurring through vibrational overtone pumping which can contribute significantly to atmospheric chemistry. Pyruvic and glyoxylic acids provided informative examples where several low energy conformers could be studied spectroscopically[1, 2]. Spectra obtained in our experimental group could be used to guide theory and obtain structural and dynamical information about these acid's overtone initiated reactions which were shown to proceed extremely rapidly (< ps) through a direct (nonstatistical) mechanism.

Water, even one water molecule, can significantly modify the photochemistry of an atmospheric chromophore. The example of pyruvic acid illustrates the different photochemical mechanisms in gas phase compared with aqueous solution. In aqueous solution polymerization occurs increasing the chemical complexity of the system. A consequence of this photochemistry is surface partitioning of reaction products, which modify the surface morphology of atmospheric aerosol particles.

Recent experimental work has explored unique properties and processes at the air-water interface. Is the water surface able to promote and enable chemistry not favorable in the bulk solution? Our work has utilized complementary surface-sensitive information from π-A isotherms, Brewster Angle Microscopy (BAM) and Infrared Reflection-Absorption Spectroscopy (IRRAS) to monitor morphological and chemical changes in organic films at the water surface. Vibrational spectroscopy allowed the *in situ* observation of condensation chemistry, specifically peptide bond synthesis occurring specifically at the air-water interface[3, 4]. The effect of water and sunlight mediated chemistry to the Earth contemporary and ancient atmosphere will be discussed.

1. K. Takahashi, K. L. Plath, R. T. Skodje and V. Vaida, *Journal of Physical Chemistry A*, 2008, **112**, 7321-7331.
2. K. Takahashi, K. L. Plath, J. L. Axson, G. C. Nelson, R. T. Skodje and V. Vaida, *J. Phys. Chem. A*, 2010, **132**, DOI: 10.1021/094305.
3. E. C. Griffith and V. Vaida, *Proceedings of the National Academy of Sciences*, 2012, **109**, 15697-15701.
4. E. C. Griffith and V. Vaida, *J. Am. Chem. Soc.*, 2013, **135**, 710-716.