

Photochemical Reaction Dynamics in the Service of Atmospheric Chemistry:  
*How the Study of Fundamental Reaction Mechanisms Can Solve Deficiencies in  
Atmospheric Models.*

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Atmospheric models provide the predictive power to assist in control, regulation and understanding of important issues such as climate change, urban pollution and the recovery of the Antarctic ozone hole. Models, of course, are only as good as the reactions comprise them. But the atmosphere is incredibly complex – over 2 billion tonnes of organic material, with over a million chemical structures, is emitted to the atmosphere every year. Models are, accordingly, also very complex; for example the Master Chemical Mechanism chemical model for the atmosphere (U. Leeds, UK) contains over 17,000 reactions. In a recent review of tropospheric chemistry, four significant weaknesses in these models were pointed out:

- i) predicting the concentration of OH radicals in forested regions;
- ii) determining the chemical processes that give rise to secondary organic aerosols;
- iii) predicting the concentration of organic acids; and
- iv) reproducing the observed concentration of H<sub>2</sub>.

Photochemical reactions carried out in a molecular beam are ideal for characterizing how the energy is deposited into the products, and the collision-free environment ensures that the reaction is a primary process. However, quantum yields are generally very difficult to measure (we know a reaction happens for sure, but not whether it is important!). Reactions in gas bulbs can be used to determine absolute quantum yields, but untangling the complex chemistry is difficult (we know how much products are formed, but not how). The combination of the two techniques can yield both mechanism and importance.

In this seminar, I will explain some of our recent studies on reaction mechanisms for laser-induced photochemistry of carbonyls, both in molecular beams and gas bulbs. The first measurement of photo-tautomerization in carbonyls leads us to hypothesize the origin of the missing organic acids in atmospheric models (iii, above). Atmospheric models also underestimate the observed amount of H<sub>2</sub> in the atmosphere (iv, above). The combination of H<sub>2</sub> production in photolysis of acetaldehyde in a beam, and ketene production in the bulb leads us to conclude that the missing H<sub>2</sub> production might arise from photochemistry of carbonyls. Finally, I will speculate on a source of OH radicals (i, above), which involves “roaming” reactions.