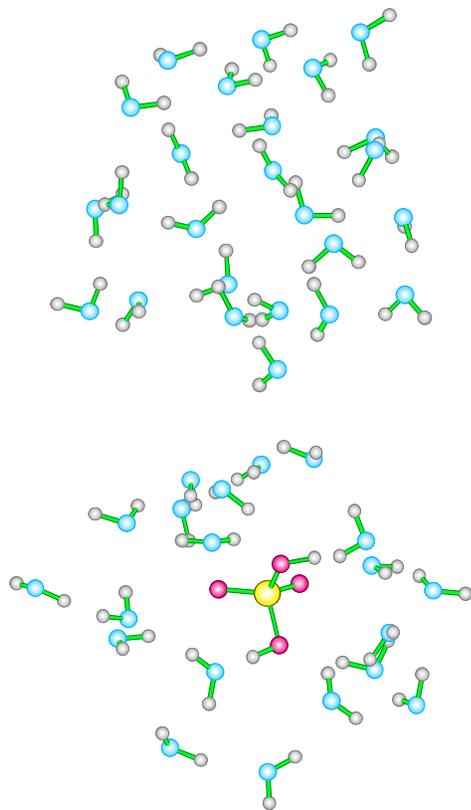


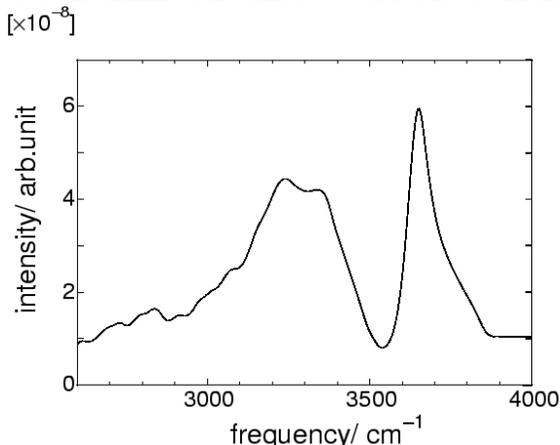
## ***Nucleation of Tropospheric Aerosols: Kinetics and Sensitivity***



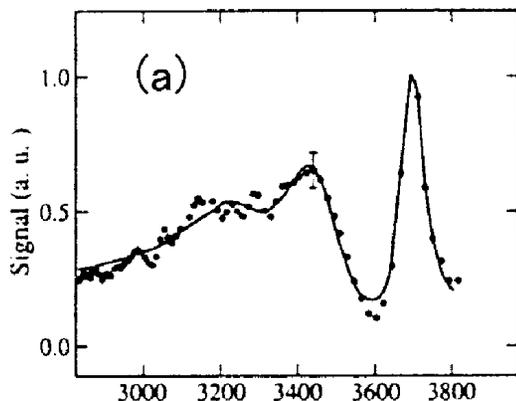
The aerosol studies involve an approach that determines homogeneous nucleation rates from knowledge of the molecular interactions that are used to define properties of molecular clusters. Over the past few years our research team developed Dynamical Nucleation Theory (DNT), which is a significant new advance in the theoretical description of homogeneous gas-to-liquid nucleation, and applied it to the nucleation of water. Sensitivity analysis of the kinetic parameters shows that the underlying interaction potentials have a profound influence on the nucleation rate. This extreme sensitivity to the cluster energetics makes the study of multi-component systems, such as sulfuric acid and water, critical.[Kathmann, Schenter, Garrett, *J. Chem. Phys.* **108** 6222 (1998); *Phys. Rev. Lett.* **82**, 3484 (1999); *J. Chem. Phys.* **111**, 4688 (1999)]

## Theory and experiment for the Sum Frequency Generation (SFG) spectrum of the water surface

J.T. Hynes



Theory: Morita and Hynes, Chem. Phys. 258 (2000) 371

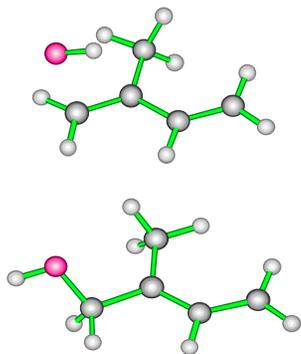
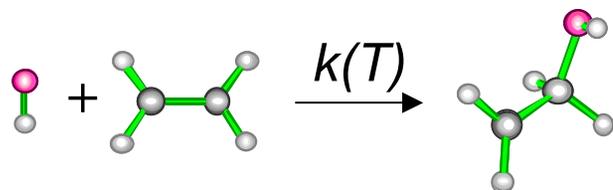


Experiment: Du et al. Phys. Rev. Lett. 70 (1993) 2313

In sum frequency generation (SFG) spectroscopy, a visible laser with fixed frequency and a tunable IR laser are employed as the two input lights, and the output intensity of the sum frequency light is detected. This nonlinear spectroscopy is quite useful to detect the interface structure since the SFG signal exclusively originates from the interface. Therefore, it provides a surface vibrational spectroscopy by tuning the IR light. The figures show the SFG spectrum of the water/vapor interface, where the IR frequency region (3000-4000 $\text{cm}^{-1}$ ) is that of the OH stretching vibrations. One of the most noticeable features is the two-band structure, consisting of the sharp band at 3700  $\text{cm}^{-1}$  and the broad band at 3000-3500  $\text{cm}^{-1}$ . The former is assigned as the surface dangling OH in the hydrogen-bond network, and the latter as the hydrogen-bonded OH at the surface. Our theoretical model successfully reproduces this overall feature and the relative intensity of the two bands. Encouraged by this success in the water case, we are planning to apply our theory to other surfaces relevant to the atmospheric aerosols to elucidate their surface structures.

EMSL UP # 1812

## Tropospheric VOC Radical Chemistry and Kinetics



Kathmann, Garrett, Dupuis

The oxidation of volatile organic compounds (VOCs) and organic sulfur compounds can form precursor molecules that form nucleation centers for aerosols. Oxidation reactions involving radicals are difficult to study both experimentally and theoretically. Radical reactions are fast, complicating the identification of important reaction pathways, especially for addition reactions with near zero barriers.. Obtaining accurate rate constants from first-principles for radical reactions is computationally challenging. High level ab initio electronic structure calculations are used to unravel the chemical reactivity of naturally occurring VOCs with the OH radical (e.g. OH+ butadiene and isoprene). Detailed mechanistic information regarding the degradation pathways and accurate reaction rate constants for key VOC reactions are being calculated.

## ***Energetics and Reactivities of Halogenated Radicals for Atmospheric Chemistry***

<b>Reaction</b>	<b><math>\Delta H(0K)</math> kcal/mol</b>
<b><math>C(O)Cl_2 \rightarrow ClCO + Cl</math></b>	<b>75.7</b>
<b><math>C(O)Cl_2 \rightarrow CO + 2Cl</math></b>	<b>81.6</b>
<b><math>COCl \rightarrow CO + Cl</math></b>	<b>5.9</b>
<b><math>C(O)Br_2 \rightarrow BrCO + Br</math></b>	<b>51.6</b>
<b><math>C(O)Br_2 \rightarrow CO + 2Br</math></b>	<b>51.9</b>
<b><math>COBr \rightarrow CO + Br</math></b>	<b>0.3</b>

"The Molecular Structures and Energetics of  $Cl_2CO$ ,  $ClCO$ ,  $Br_2CO$ , and  $BrCO$ ". D.A. Dixon, K.A. Peterson, and J.S. Francisco, *J. Phys. Chem. A*. **2000**, *104*, 6227

The halogenated derivatives of formaldehyde have been postulated to play a role in the chemistry of the upper troposphere and in the stratosphere. Given the potential importance of these compounds, there are few reliable studies of the energetics of these compounds, especially for radicals such as XCO where X is a halogen. The heats of formation of  $ClCO$ ,  $Cl_2CO$ ,  $BrCO$ , and  $Br_2CO$  have been calculated at high levels of *ab initio* molecular orbital theory. With the calculated  $\Delta H_f$ 's, the atmospheric fate of the  $ClCO$  and  $BrCO$  radicals can be addressed, especially with respect to reactions in the stratosphere. An interesting conclusion regarding the atmospheric oxidation of  $C(O)Cl_2$  and  $C(O)Br_2$  can be reached. Photolysis of these compounds in the stratosphere leads to the formation of CO and the release of either two chlorine atoms or two bromine atoms, which could participate in catalytic ozone destruction cycles.

# ***GC-2 Highlights***

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