

Vibrational Pre-Reactivity: Exploiting Complexes to Probe Reactive Resonances

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This project aims to explore the dynamics ensuing from reactive resonances in bimolecular reactions. We first prepare atom-molecule van der Waals complexes and then use tunable infrared radiation to optically prepare the resonance states. The resonance states can subsequently decay by predissociation (returning to reactants) or prereaction (forming products), and the dynamics of these processes will be explored by using velocity-map imaging (VMI) to measure the correlated product state distributions.

At the end of the last reporting period we had completed modifications to the VMI mass spectrometer to allow photolysis of atom or radical precursor species in the throat of the supersonic expansion, prior to the skimmer. Experiments designed to explore the viability of SOCl_2 as a Cl atom precursor were underway. While our conclusion was ultimately that it is likely to be problematic if used as a precursor, we were able to make measurements exploring three-body dissociation of SOCl_2 , probing Cl/Cl^* atoms and SO radicals. Cl and Cl^* atoms are detected readily in one-color experiments performed near 235 nm, where the frequency-doubled output of a Nd:YAG-pumped dye laser induces photolysis and detects the Cl/Cl^* atoms by 2+1 resonance-enhanced multiphoton ionization. The branching fraction for production of spin-orbit excited Cl^* atoms was found to be 0.29 ± 0.05 . Both spin-orbit states are produced with trimodal speed distributions (see Figure 1). An apparently ‘thermal’ component characterized by a temperature of ~ 1000 K is accompanied by two highly anisotropic fast components. While the overall distributions are similar, the relative contributions from each component are significantly different. The ‘thermal’ component is non-statistical, however, and shows some degree of anisotropy and is likely due to three-body fragmentation. Qualitatively similar behavior is observed in ion images of the SO fragment, probed by 1+1 REMPI on the $d-\text{X}(0,1)$ and $(0,2)$ bands near 235 nm and 242 nm, respectively. Analysis of these data is in progress.

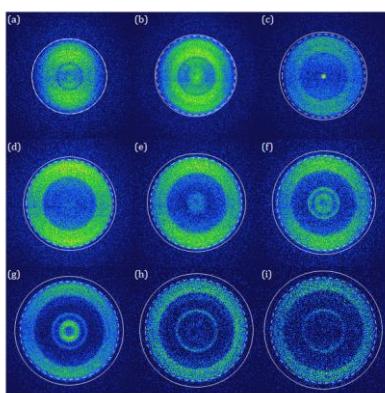


Figure 2 SO^+ ion images arising from two-photon dissociation of SO_2 . Images (a)–(i) span the wavelength range 222–208 nm.

required been operational and we have been forced to spend a considerable amount of time on diagnostics and repairs. Both KTP crystals in the non-resonant oscillator stage of the IR optical parametric oscillator were damaged and had to be replaced. The external triggering electronics of the seeded Nd:YAG pump laser also failed, preventing synchronization with the other laser systems. The manufacturer was unable to provide any technical support, which prolonged the length of time required for diagnostics. Ultimately, we replaced all the chips on the integrated circuit

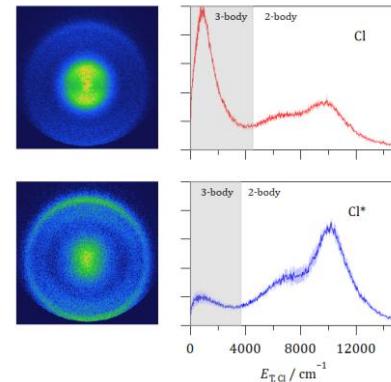


Figure 1 Cl and Cl^* ion images and translational energy distributions. Shaded areas indicate products of three-body dissociation.

While working with SOCl_2 at wavelengths < 225 nm, we observed a series of sharp resonances leading to formation of SO^+ cations. We were ultimately able to assign the spectrum to vibrational progressions of the $\tilde{\text{C}}^1\text{B}_2-\tilde{\text{X}}^1\text{A}_1$ transition of SO_2 , presumably present as a minor contaminant in the gas manifold. Ion images of SO^+ obtained with the laser fixed on these resonances in the range 225–208 nm are shown in Figure 2. The images comprise broad pairs of rings that increase in radius as the available energy increases, with sharper slow features present at some wavelengths. The $\tilde{\text{C}}$ state of SO_2 can predissociate to $\text{SO} + \text{O}(\text{P})$ at wavelengths less than < 219 nm, but several lines are observed below this threshold. Our current interpretation is that electronically excited SO $\text{A}^3\Pi$ and $\text{B}^3\Sigma^-$ are formed in a two-photon dissociation that is resonance-enhanced at the one photon level. Absorption of a third photon leads to ionization of the electronically excited SO radicals.

In the last report, various technical problems were described that had hindered progress towards the primary goal. Unfortunately, we have continued to struggle in this regard. At no point has all of the equipment

board and resolve the external triggering problem. Most recently, the Roots pumps backing the turbomolecular pumps on the VMI apparatus either failed or showed signs of imminent failure in quick succession. We have replaced the failed pump using other funding sources, and but are still awaiting completion of repairs on the other. As soon as that pump is returned, we will be in a position to resume experiments.