CHARACTERIZATION OF STRUCTURAL MOTIFS FOR $CO_2$ ACCOMMODATION BY IONIC SPECIES RELEVANT TO PHOTOELECTROCATALYSIS USING CRYOGENIC VIBRATIONAL PREDISSOCIATION SPECTROSCOPY

JOSEPH A. FOURNIER, CHRISTOPHER J. JOHNSON, CONRAD T. WOLKE, ARRON B. WOLK, CHRISTOPHER M. LEAVITT, KRISTEN J. BREEN, and MARK A. JOHNSON, *DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CT 06520*.

Two aspects of catalytic $CO_2$ conversion to transportable fuels involve understanding the local interactions between $CO_2$ and the solvent mediating the reduction and the coordination of $CO_2$ onto the organometallic framework that executes the chemical transformation. To address why ionic liquids are emerging as the solvents of choice for the catalysis, we first explore how $CO_2$ attaches to two archetypal ionic liquid components: imidazole (Im) and acetate ($Ac^-$). Im was seeded in a $CO_2$ pulsed free jet expansion forming $Im(CO_2{}^-)(CO_2)_m$ (m=1-2) clusters. Previous studies with pyridine revealed C-N bond formation between $CO_2{}^-$ and pyridine with m=5 or 7, evidenced by the observation of a C-N stretch in the vibrational spectra. No such C-N bond formation is observed with Im; the $CO_2{}^-$ appears to be hydrogen bonded to the Im N-H in an ion-molecule complex. Attachment to $Ac^-$ was studied by predissociation of the $Ac^-(CO_2)_m$ (m=1-4) clusters and, for m=1-3, a single peak assigned to the $CO_2$ asymmetric stretch is observed near that of bare $CO_2$, suggesting that the $CO_2$ molecules are weakly bound adducts. However, the combination bands $2\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ in the $3600 - 3750\mathrm{cm}^{-1}$ region reveal two distinct binding sites: a neutral site and a red-shifted, more perturbed site. For m=4, a red-shifted $CO_2$ asymmetric stretch is observed, perhaps indicating the beginning of solvent mediated activation of a $CO_2$ adduct.

Finally, the $CO_2$ reduction catalyst $Ni(cyclam)^{2+}$ has been investigated using an electrospray ionization source coupled to a cryogenically cooled ion trap. By adding $CO_2$ to the He buffer gas used to collisionally cool the ions in the trap, we have been able to condense up to five $CO_2$ molecules onto $Ni(cyclam)^{2+}$ at a trap temperature of 100K. The cryogenic ion vibrational predissociation (CIVP) spectra show the $CO_2$ molecules to be acting as neutral adducts. We are now working to develop a method to generate and isolate the reactive $Ni(cyclam)^+$ and capture the bound-$CO_2$ intermediate.