

## CHARACTERIZATION OF STRUCTURAL MOTIFS FOR CO<sub>2</sub> 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<sub>2</sub> conversion to transportable fuels involve understanding the local interactions between CO<sub>2</sub> and the solvent mediating the reduction and the coordination of CO<sub>2</sub> 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<sub>2</sub> attaches to two archetypal ionic liquid components: imidazole (Im) and acetate (Ac<sup>-</sup>). Im was seeded in a CO<sub>2</sub> pulsed free jet expansion forming Im(CO<sub>2</sub><sup>-</sup>)(CO<sub>2</sub>)<sub>m</sub> (m=1-2) clusters. Previous studies with pyridine revealed C-N bond formation between CO<sub>2</sub><sup>-</sup> 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<sub>2</sub><sup>-</sup> appears to be hydrogen bonded to the Im N-H in an ion-molecule complex. Attachment to Ac<sup>-</sup> was studied by predissociation of the Ac<sup>-</sup>(CO<sub>2</sub>)<sub>m</sub> (m=1-4) clusters and, for m=1-3, a single peak assigned to the CO<sub>2</sub> asymmetric stretch is observed near that of bare CO<sub>2</sub>, suggesting that the CO<sub>2</sub> molecules are weakly bound adducts. However, the combination bands  $2\nu_2 + \nu_3$  and  $\nu_1 + \nu_3$  in the 3600 – 3750cm<sup>-1</sup> region reveal two distinct binding sites: a neutral site and a red-shifted, more perturbed site. For m=4, a red-shifted CO<sub>2</sub> asymmetric stretch is observed, perhaps indicating the beginning of solvent mediated activation of a CO<sub>2</sub> adduct.

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