

CHARACTERIZATION OF STRUCTURAL MOTIFS FOR CO₂ ACCOMMODATION BY IONIC SPECIES RELEVANT TO PHOTOELECTROCATALYSIS USING CRYOGENIC VIBRATIONAL PREDISSOCIATION SPECTROSCOPY

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Two aspects of catalytic CO₂ conversion to transportable fuels involve understanding the local interactions between CO₂ and the solvent mediating the reduction and the coordination of CO₂ 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 CO₂ attaches to two archetypal ionic liquid components: imidazole (Im) and acetate (Ac⁻). Im was seeded in a CO₂ pulsed free jet expansion forming Im(CO₂⁻)(CO₂)_m (m=1-2) clusters. Previous studies with pyridine revealed C-N bond formation between CO₂⁻ 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 CO₂⁻ 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⁻(CO₂)_m (m=1-4) clusters and, for m=1-3, a single peak assigned to the CO₂ asymmetric stretch is observed near that of bare CO₂, suggesting that the CO₂ molecules are weakly bound adducts. However, the combination bands $2\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ in the 3600 – 3750cm⁻¹ region reveal two distinct binding sites: a neutral site and a red-shifted, more perturbed site. For m=4, a red-shifted CO₂ asymmetric stretch is observed, perhaps indicating the beginning of solvent mediated activation of a CO₂ adduct.

Finally, the CO₂ reduction catalyst Ni(cyclam)²⁺ has been investigated using an electrospray ionization source coupled to a cryogenically cooled ion trap. By adding CO₂ to the He buffer gas used to collisionally cool the ions in the trap, we have been able to condense up to five CO₂ molecules onto Ni(cyclam)²⁺ at a trap temperature of 100K. The cryogenic ion vibrational predissociation (CIVP) spectra show the CO₂ 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-CO₂ intermediate.