

## VIBRATIONAL SHIFT OF ADSORBED CARBON DIOXIDE WITHIN A METAL-ORGANIC FRAMEWORK

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There is much interest in a class of materials known as Metal-Organic Frameworks (MOFs). While practical applications center on hydrogen storage and carbon sequestration, these highly porous, crystalline materials also provide an excellent opportunity for performing matrix isolation experiments. In this talk we will present data on MOF-74, a honey-comb structure consisting of metal-oxide units linked by aromatic rings. Infrared spectra show that for a series of different metal cations,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  the vibrational modes of adsorbed  $\text{CO}_2$  are all red shifted relative to the gas phase values. In contrast the  $\nu_3$  mode of  $\text{CO}_2$  adsorbed within the Mg version of MOF-74 is unique in showing a blue shift. It is accompanied by broader sidebands associated with librational or center of mass motion of the adsorbed  $\text{CO}_2$ . Spectra obtained below 100 K show the emergence of a second  $\nu_3$  band indicating a further distortion of the  $\text{CO}_2$  molecule. These results will be discussed in terms of the interaction mechanisms of the different metal cations and in particular the fact that the Mg version of MOF-74 has a very strong affinity for  $\text{CO}_2$  with a binding energy of 47 kJ/mol, more than 5 kJ/mol greater than any other MOF.