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, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} the vibrational modes of adsorbed CO_2 are all red shifted relative to the gas phase values. In contrast the ν_3 mode of 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 CO_2. Spectra obtained below 100 K show the emergence of a second ν_3 band indicating a further distortion of the 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 CO_2 with a binding enenergy of 47 kJ/mol, more than 5 kJ/mol greater than any other MOF.