Dynamic chemical bonds reversibly break and reform with minimal heat, light, or pressure. This type of bonding is responsible for the basic mechanism of crystallization for many material systems because erroneous bond formation can be corrected through facile reversal until the material settles into the most favorable crystalline phase. A particularly important class of crystalline materials that emerge from this dynamic process are metal-organic frameworks (MOFs). MOF architecture is dependent on two building blocks: the metal ions or metal clusters and the organic ligands that bridge the metals. MOFs find applications in fields ranging from industry to medicine and determining their bridge the metals. MOFs contain metal-ligand bonds that remain dynamic throughout; we hypothesize that metal-carboxylate stretches that connect the building blocks of the frameworks can be observed by temperature-dependent Diffuse Reflectance IR spectroscopy. Shown above is the symmetric vibrational mode of C-O in MIL-125.

**Results**

Variable temperature vibrational spectroscopy shows a lowering in energy of the stretches associated with dynamic bonds at increased temperatures, indicative of bond weakening.

**Discussion**

A wide variety of common MOFs were examined to establish quantitative relationship between MOF metal-linker bond dynamicity and material composition. Other systems with varying metal ions and linkers (MIL-101, MUV-10 (Ca), MUV-10 (Mn), Mg-MOF-74, MOF-5, MIL-125-NH2, UiO-66, and sodium benzoate) were additionally analyzed and all have shown to possess the carboxylates with redshifting character with greater temperatures. Most shifts are reversible and dependent on the identity of metal and ligand.

The dynamic building principle behind metal-organic frameworks presents a fascinating platform to explore and establish interesting structure-property relations. By understanding this relationship, more general insights can be made regarding important material behavior such as crystallization and self-healing responsiveness. Insight into their labile nature would provide a predictive model of their growth mechanism and inspire important applications such as the use of MOFs for self-healing conductive membranes or as smart materials as well as how dynamic bonding impacts the behavior of robust materials overall.

**Methods**

To understand this metal-ligand interaction, our research focuses on monitoring the changes in the vibrational frequencies as a function of temperature.

The dynamicity of metal-carboxylate stretches that connect the building blocks of the frameworks can be observed by temperature-dependent Diffuse Reflectance IR spectroscopy. The wavenumber of the vibrational mode changes with respect to temperature. Opaque markers are the values fitted to a Gaussian function and transparent markers are the experimental values.

**Background**

Dynamic chemical bonds reversibly break and reform with minimal heat, light, or pressure. This type of bonding is responsible for the basic mechanism of crystallization for many material systems because erroneous bond formation can be corrected through facile reversal until the material settles into the most favorable crystalline phase. A particularly important class of crystalline materials that emerge from this dynamic process are metal-organic frameworks (MOFs). MOF architecture is dependent on two building blocks: the metal ions or metal clusters and the organic ligands that bridge the metals. MOFs find applications in fields ranging from industry to medicine and determining their bridge the metals. MOFs contain metal-ligand bonds that remain dynamic throughout; we hypothesize that metal-carboxylate stretches that connect the building blocks of the frameworks can be observed by temperature-dependent Diffuse Reflectance IR spectroscopy. Shown above is the symmetric vibrational mode of C-O in MIL-125.

**Hypothesis and Model**

For the past two decades, MOFs have been viewed as rigid structures, but we propose that even after formation, MOFs contain metal-ligand bonds that remain dynamic such that the crystalline structure contains mixtures of partially bound and unbound arrangements.

We hypothesize that metal-carboxylate bonds — which constitute the majority of MOFs — are especially dynamic, with large fraction of these bonds existing in unbound states.

**Suppose two “states”**

- **Strong bonding**
  - Global Fit
  - $A = B \Delta H > 0$
- **Weak bonding**
  - $A > B$

**Higher T, more B, smaller wavenumber**

**References**