Brozek group

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Metal-Ligand Bond Dynamics in Metal-Organic Frameworks Confirmed by Variable Temperature Vibrational Spectroscopy

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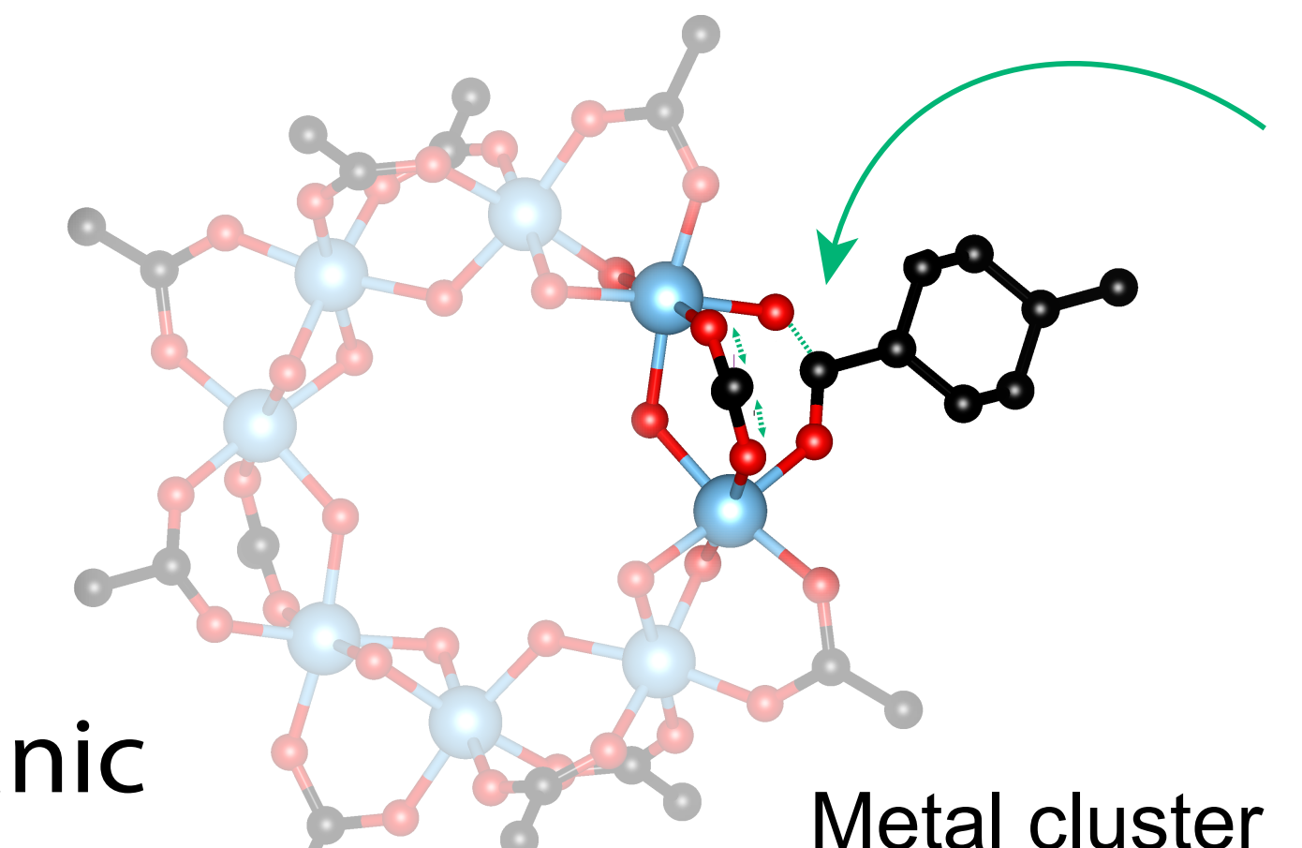
Background

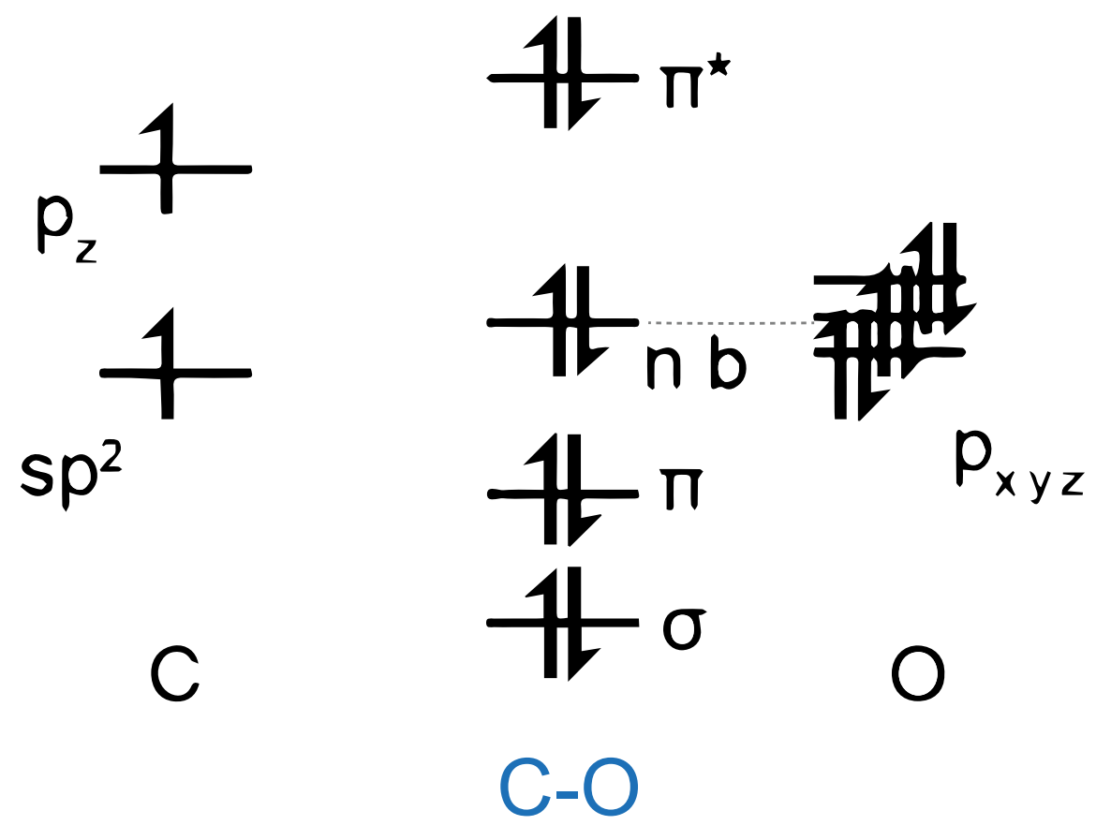
Dynamic chemical bonds reversibly break and reform with minimal heat, light, or pressure. This type of bonding is responsible for the basic mechanism of crystallization for many material systems because erroneous bond formation can be corrected through facile reversal until the material settles into the most favorable crystalline phase.[1] 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[2,3] and determining their mechanistic behavior (such as phase transitions, growth mechanism) would be essential to answering basic science questions relating to structure-property relationships.[4]

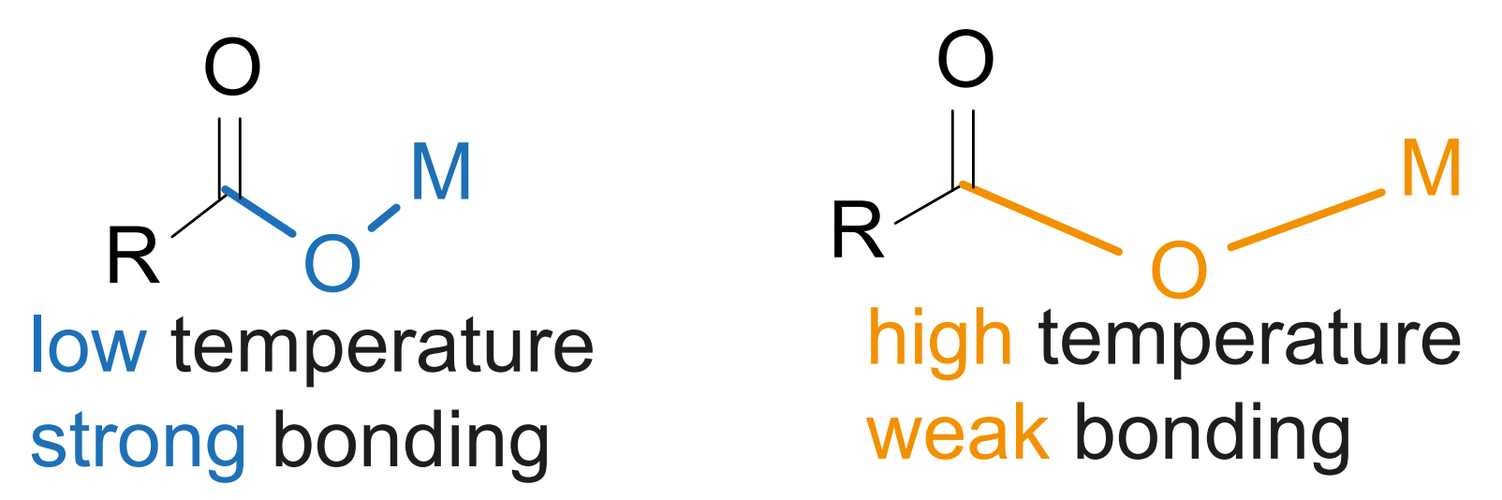


Metal cluster of MIL-125

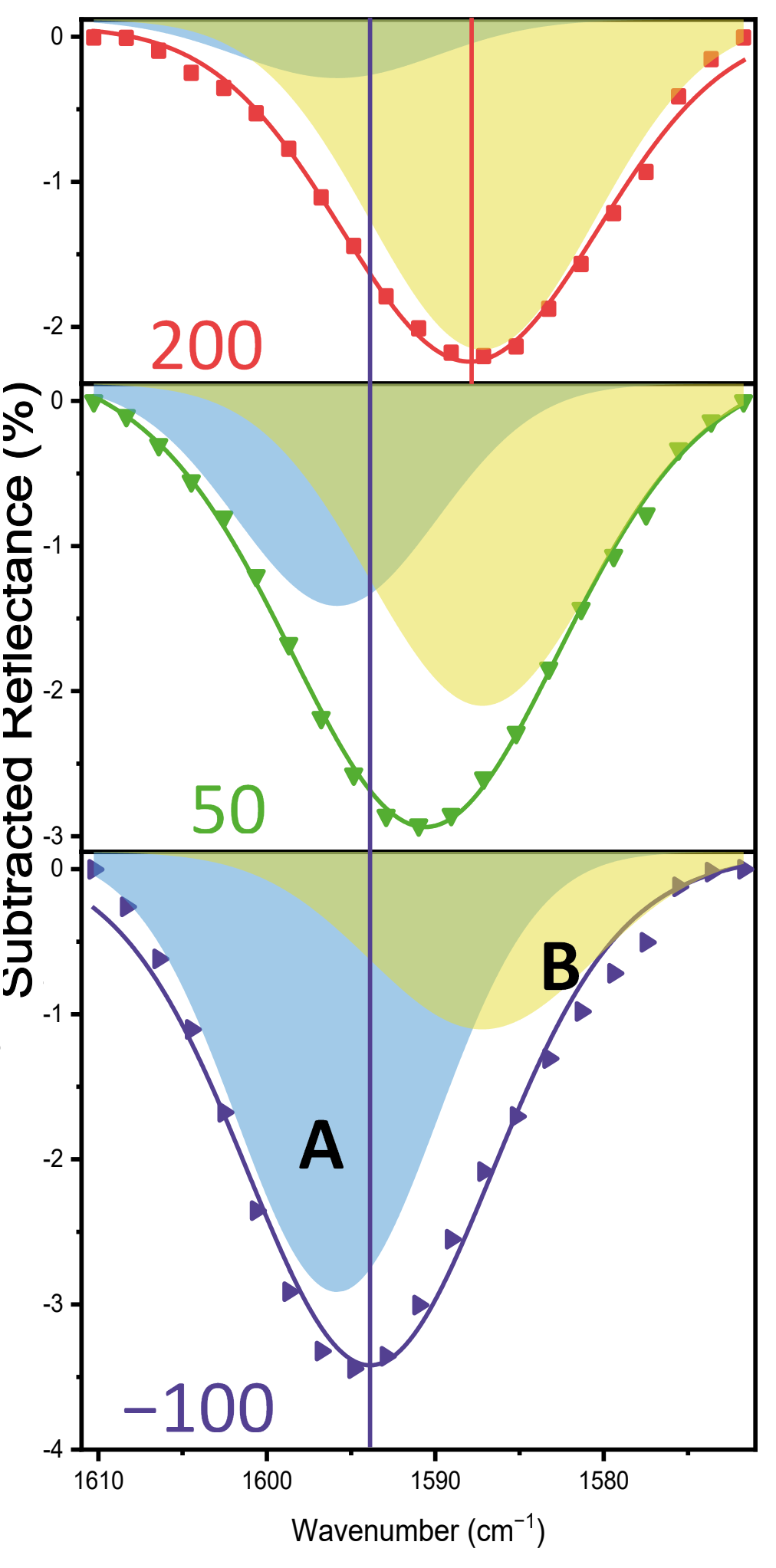
Hypothesis and Model

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"

$A \rightleftharpoons B$ $\Delta H > 0$

$\nu_A > \nu_B$

Higher T, more B, smaller wavenumber

- Global Fit

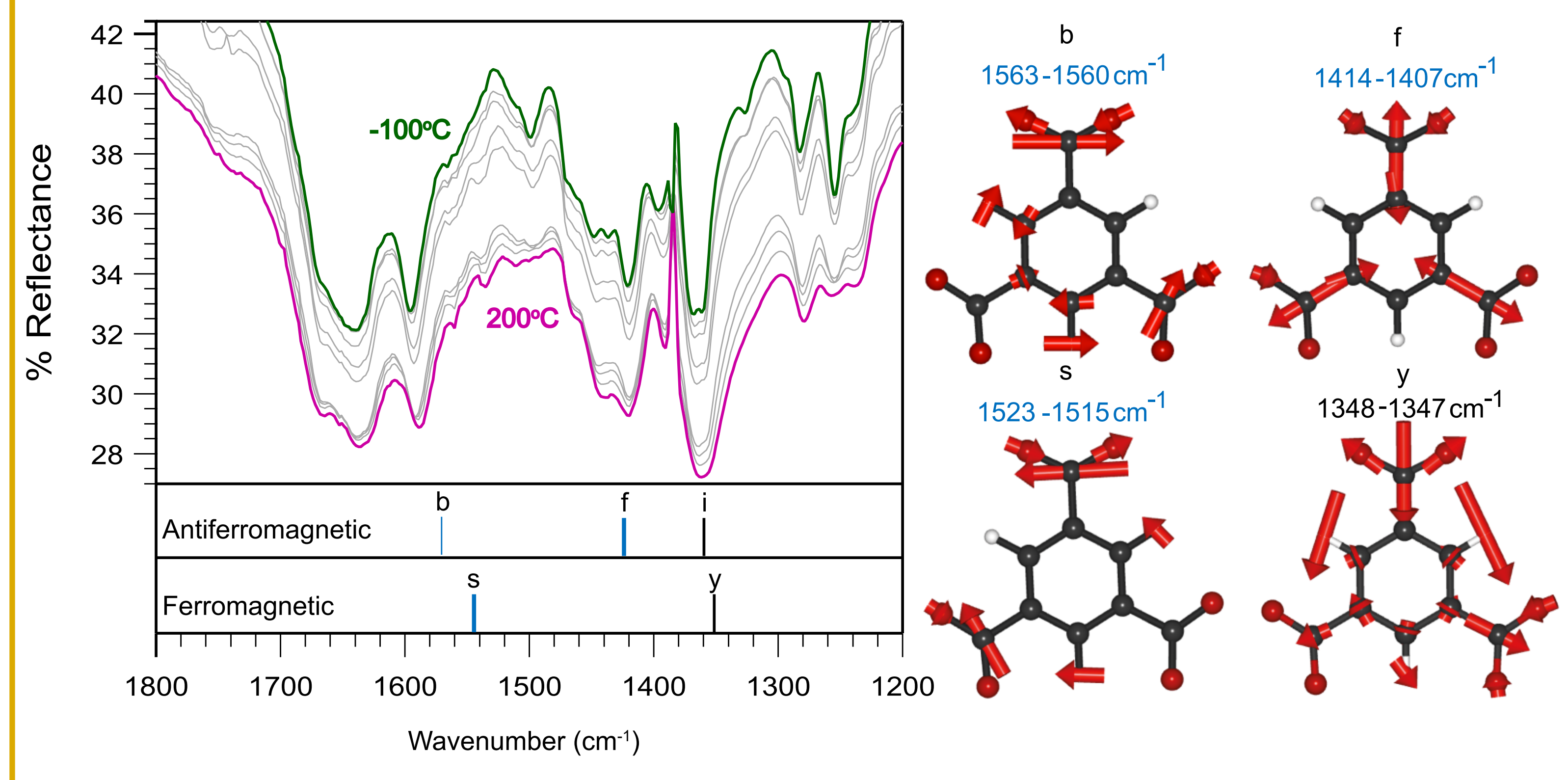
  $\nu_A = 1595.8 \pm 0.1\ \text{cm}^{-1}$

  $\nu_B = 1587 \pm 1\ \text{cm}^{-1}$

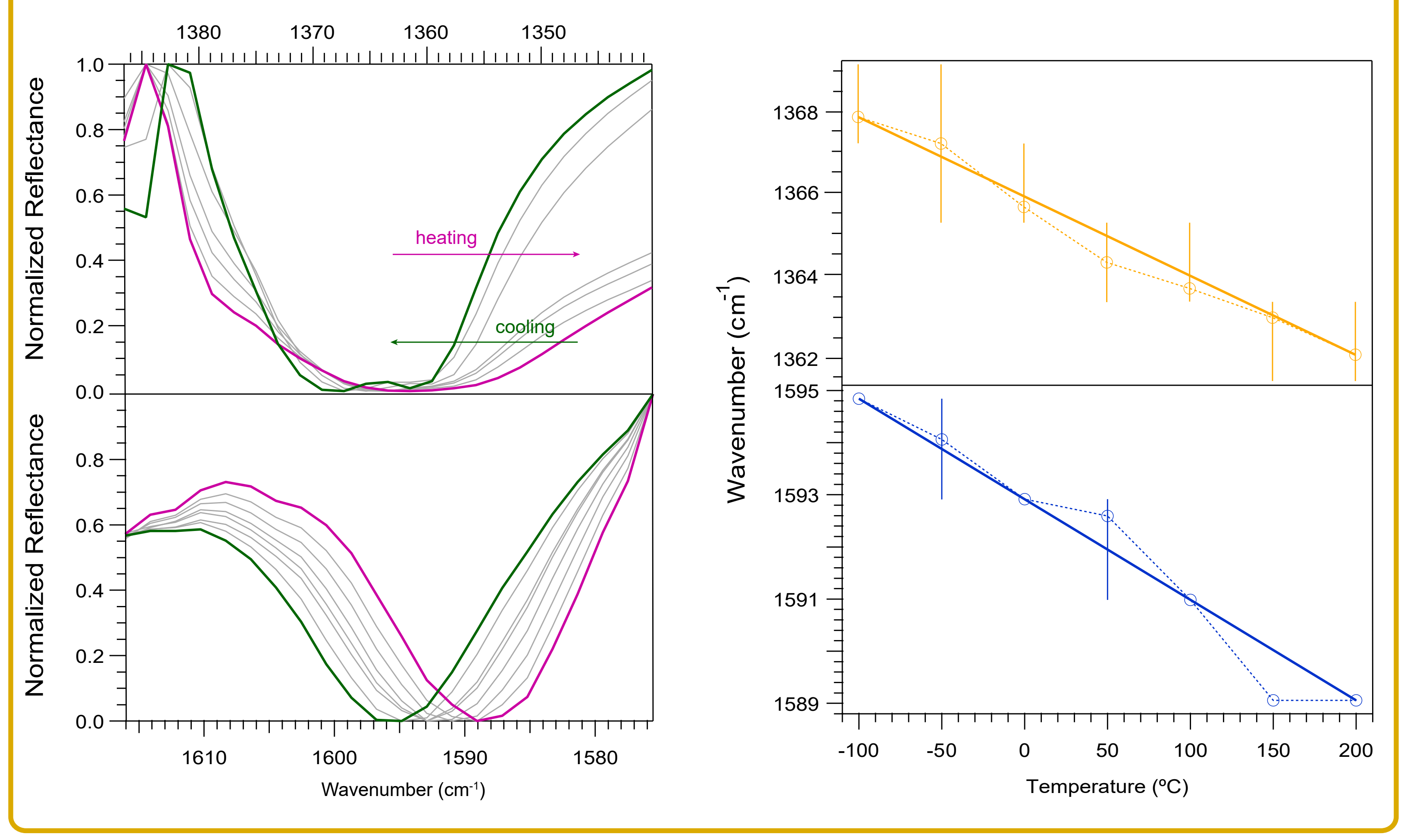
- Define

  K = Area(B) / Area(A)

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

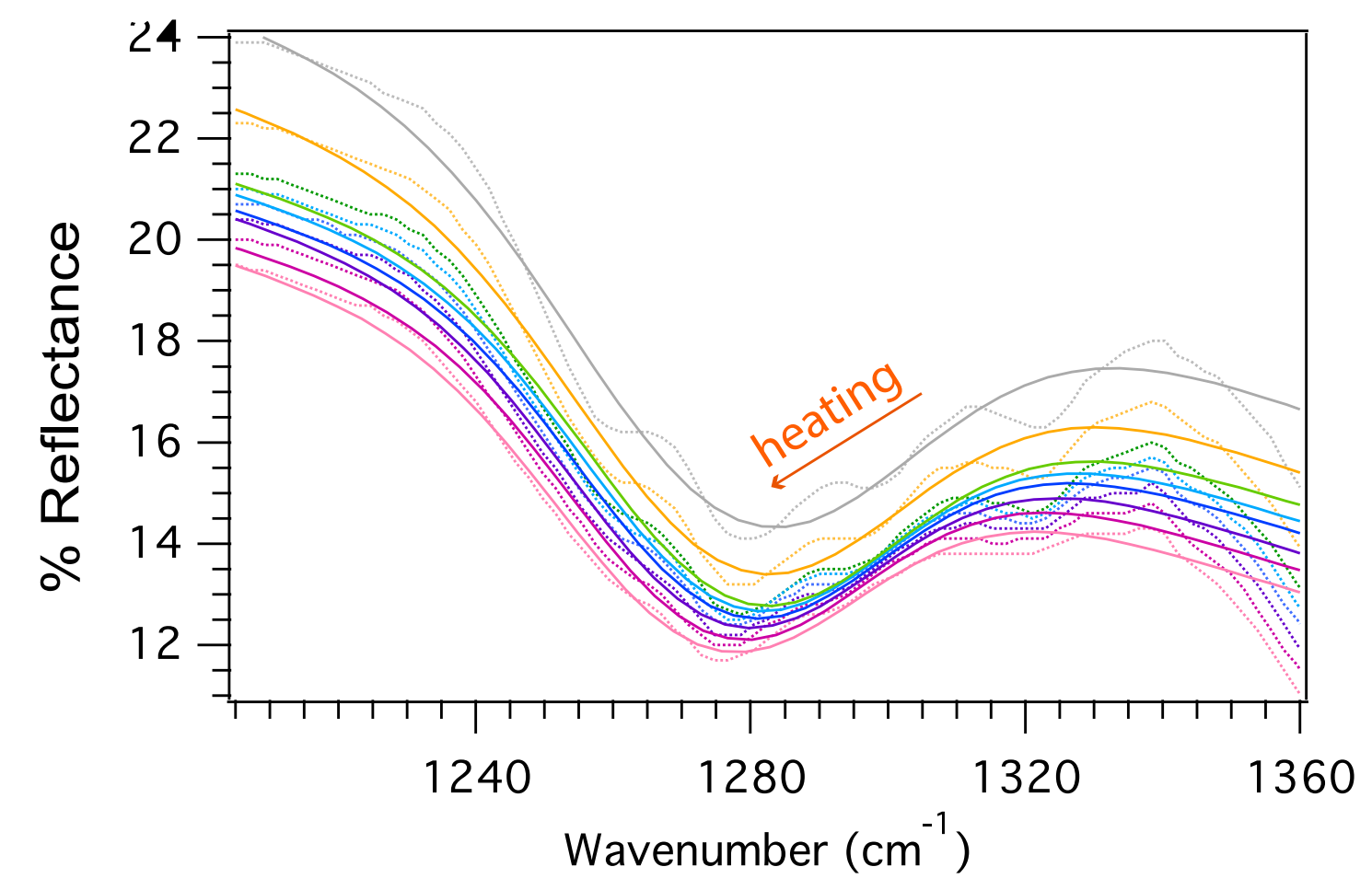
A wide variety of common MOFs were examined to establish quantitative relationship between MOF metal-linker bond dynamicity and material composition. 8 other systems with varying metal ions and linkers (MUV-10 (Ca), MUV-10 (Mn), Mg-MOF-74, MOF-5, MIL-125, MIL-125-NH2, UiO-66, and sodium benzoate) were 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.

	v_8 (cm^{-1})	v_3 (cm^{-1})	v_8 shift (cm^{-1})	v_3 shift (cm^{-1})	Δv (cm^{-1})
CuBTC	1590	1363	5.785	5.785	227
MUV-10 (Ca)	1640	1340	7.714	5.303	300
MUV-10 (Mn)	1620	1330	2.1	7.1	290
Mg-MOF-74	1580	1370	3.514	1.929	210
MOF-5	1590	1435	3.857	1.6	155
MIL-125	1590	1398	4.339	7.231	192
MIL-125-NH$_2$	1590	1382	1.935	-	208
UiO-66	1585	1400	3.857	5.785	185
Sodium benzoate	1552	1419	4.821	6.749	133

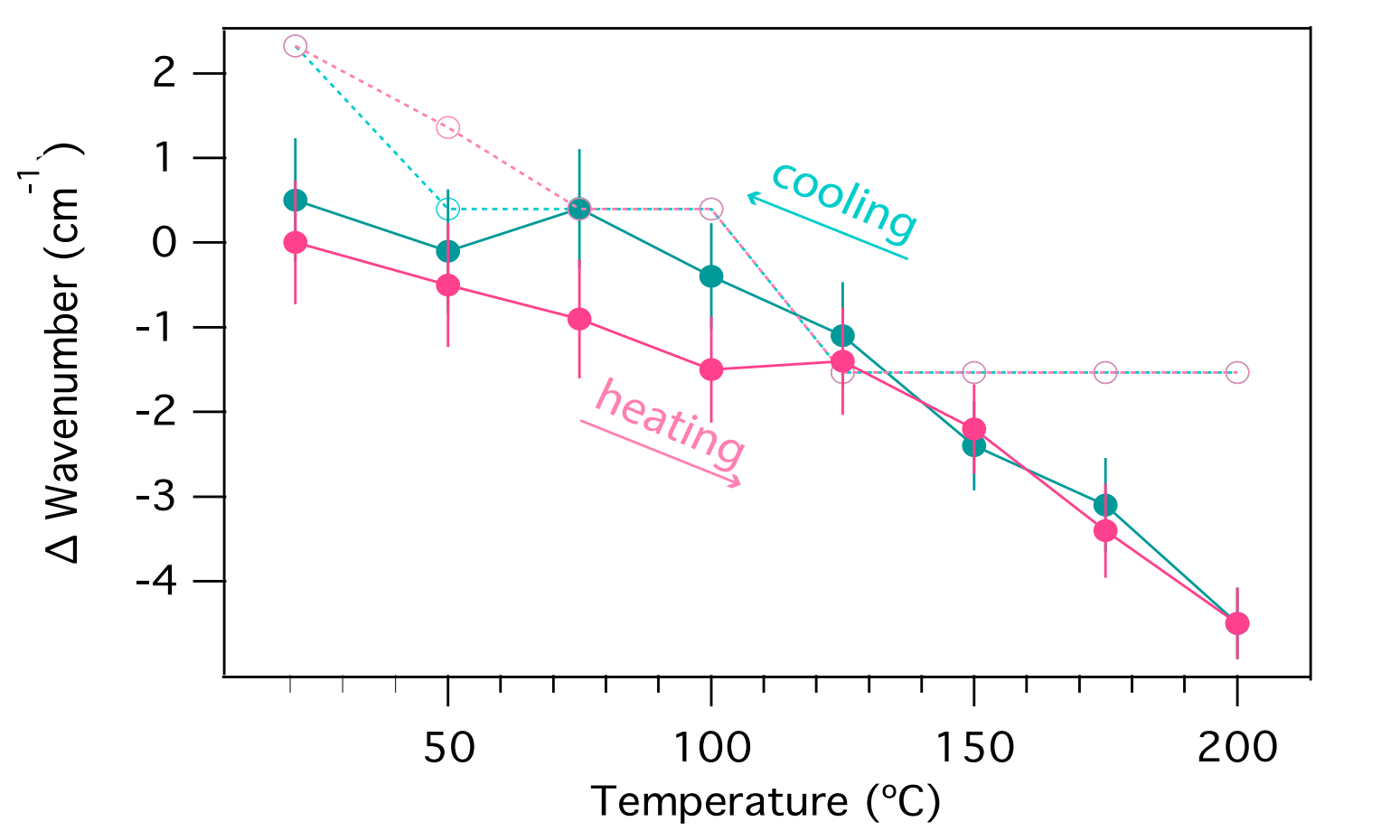
The dynamic building principle behind metal-organic frameworks presents a fascinating platform to explore and establish interesting structure-property relations.[5] By understanding this relationship, more general insights can be made regarding important material behavior such as crystallization and 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. Shown above is the symmetric vibrational mode of C-O in MIL-125.



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.

References

1. Howarth, A. J., Peters, A., Vermeulen, N., Wang, T., Hupp, J., and Farha, O. Best Practices for the Synthesis, Activation, and Characterization of Metal-Organic Frameworks. Chem. Mater., 2016, 29, 26-39.
2. Li, P., Li J., Feng, X., Li, J., Hao, Y., Zhang, J., Wang, H., Yin, A., Zhou, J., Ma, X., and Wang, B. Metal-organic frameworks with photocatalytic bactericidal activity for integrated air cleaning. Nat. Com., 2019, 10 (1), 2177.
3. Gong, X., Noh, H., Gianneschi, N. C., and Omar K. Farha. Interrogating Kinetic versus Thermodynamic Topologies of Metal–Organic Frameworks via Combined Transmission Electron Microscopy and X-ray Diffraction Analysis. J. Am. Chem. Soc., 2019, 141, 15, 6146-6151.
4. Redfern, L. R., Farha, O. K. Mechanical properties of metal-organic frameworks. Chem. Sci., 2019, 10, 10666.
5. Gaillac, R., Pullumbi, P., and Coudert, F.-X. Melting of Zeolitic Imidazolate Frameworks with Different Topologies: Insight from First-Principles Molecular Dynamics. J. Phys. Chem. C, 2018, 122, 6730–6736.

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