

The goal of this project is to use two-dimensional IR spectroscopy (2D-IR) to study adsorbed CO<sub>2</sub> inside of MOF materials to monitor the fast configurational rearrangements during the course of an adsorption isotherm. Using this methodology, we will ultimately study a series of isostructural MOFs with different open metal binding sites for CO<sub>2</sub> to determine the effect of the metal identity on time dependent structural motions of the adsorbed gas. We will also study a set of structurally similar MOFs that offer varying degrees of flexibility during gas adsorption

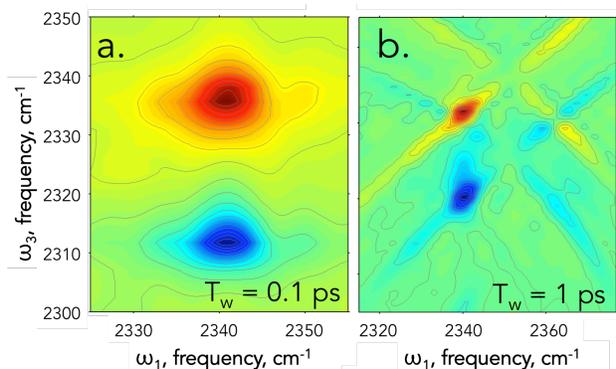
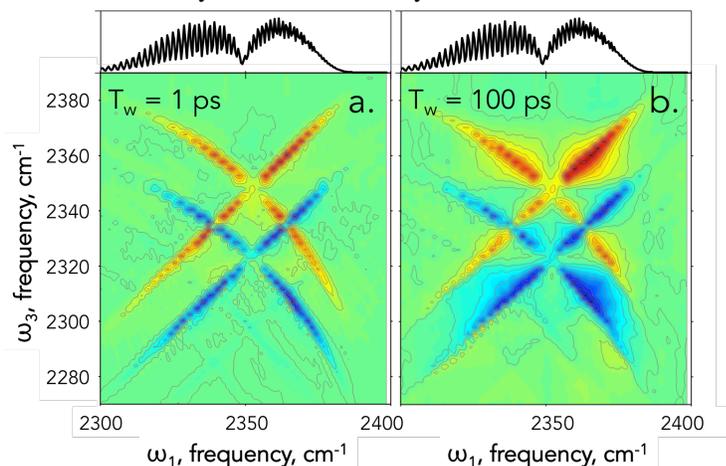
to determine the impact of framework mobility on CO<sub>2</sub> configurational dynamics, and will expand this work to also investigate the influence of hydration. These studies will generate experimental data in the form of frequency-frequency correlation functions (FFCF) that characterize the molecular dynamics and are directly comparable to FFCFs obtained from simulations.

During this funding period, significant progress was made toward the research objectives. The 2D-IR spectra for gas-phase CO<sub>2</sub> were collected at a range of waiting times ( $T_w$ ) so that we could characterize the behavior of this background signal that will be present in MOF measurements. Figure 1 shows the 2D-IR spectra for the asymmetric stretching vibration at a short (1 ps) and long (100 ps) waiting time for a sample that had a partial pressure of CO<sub>2</sub> of ~1 milli-atm diluted in nitrogen to 1 atm. Rotational peaks are resolved in the 2D-IR spectrum. The spectra have a characteristic “x” shape that indicates that there is strong correlation between the P- and R-branches of the rotational spectrum

**Figure 1.** 2D-IR spectra of gas phase CO<sub>2</sub> diluted to 1 atm in nitrogen and recorded at waiting times of a)  $T_w = 1$  ps and b)  $T_w = 100$  ps. Overlaid at the top of each frame is the FTIR spectrum of CO<sub>2</sub> for reference.

with the same rotational quantum number ( $J$ ). This type of 2D-IR spectrum was recently reported by Mandal and coworkers for a high pressure N<sub>2</sub>O sample<sup>1</sup> but has not been previously shown for CO<sub>2</sub>. Mandal and coworkers reported that there was a loss of correlation of  $J$ -states after tens of ps due to just a few molecular collisions.<sup>1</sup> At our pressure the average time between collisions is approximately 200 ps leading to very little  $J$ -state scrambling by 100 ps. We also measured the vibrational lifetime of the CO<sub>2</sub> to be fairly long at ~80 ps. The conclusions from these spectra are that the background 2D-IR signal from gas phase CO<sub>2</sub> in MOF sample will be unique and long-lived. This should enable us to remove it as a background spectral feature in future work.

We initiated measurements of CO<sub>2</sub> adsorbed to the inner surfaces of organic materials. Initial studies in this funding period focused on CO<sub>2</sub> adsorbed inside of polymeric membranes as these provide a simple flexible surrogate of the more rigid structures in MOF materials. Poly(dimethylsiloxane) (PDMS) and poly(methylmethacrylate) (PMMA) were chosen to represent two different dynamic regimes. PDMS is above its glass transition at room temperature, thereby enabling a wide range of structural dynamics of the organic scaffold to which CO<sub>2</sub> adsorbs. In contrast,

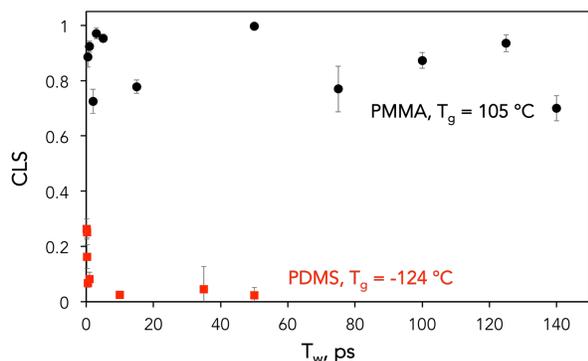


**Figure 2.** 2D-IR spectra of CO<sub>2</sub> adsorbed to the interior surfaces of a) PDMS and b) PMMA, both at relatively short  $T_w$  times. Frequency axes extended for PMMA to show presence of CO<sub>2</sub> gas features.

PMMA is below its glass transition at room temperature and is fairly brittle and dynamically limited. Furthermore, PMMA offers the possibility of specific molecular binding of the gaseous guest molecule, akin to what might be experienced inside a MOF. Representative 2D-IR spectra are shown for the asymmetric stretch of CO<sub>2</sub> inside PDMS (Fig. 2a) and PMMA (Fig. 2b) at short waiting times. It is clear that the CO<sub>2</sub> vibration looks very different in an adsorbed state than it did above in the gas phase. The peaks in both frames show a single peak of condensed phase, adsorbed CO<sub>2</sub> interacting non-specifically with the organic matrix material. The spectrum is shown for PMMA with expanded axes to highlight the presence of gas-phase CO<sub>2</sub> signal in the background, as shown above. The PDMS sample lacked this background, which we attribute to the fact that the PMMA is brittle and semicrystalline and likely has microscopic void regions in which the CO<sub>2</sub> gas can reside.

The 2D peak shapes are notably different between these two samples. In PDMS, the peak shapes are fairly round, while they are elongated along the diagonal in PMMA. This indicates that the chemical environment in PMMA is heterogeneous and that the dynamics are slow, preventing interconversion of environments on the 1 ps timescale. We measured longer waiting time spectra for these same samples and found that the line shapes were nearly invariant. To characterize these dynamics (or lack thereof) we analyzed 2D-IR spectra using the centerline slope (CLS) approach. The centerline is defined by fitting vertical slices across the 2D-IR peak to find their maxima. The PDMS line shapes in Fig. 2a would have a centerline that is nearly horizontal, giving a CLS that is nearly zero. The PMMA peak in Fig 2b would have a centerline that is nearly 45°, giving a CLS that is nearly 1. Monitoring the evolution of the CLS with T<sub>w</sub> enables one to determine the time scales of interconversion of chemical environments,

as would be expected for CO<sub>2</sub> bound inside an organic material.



**Figure 3.** Centerline slopes (CLS) for CO<sub>2</sub> asymmetric stretch in PDMS (red markers) and PMMA (black markers).

The CLS values for PDMS and PMMA are shown in Figure 3. In PDMS, the peak shape reaches its nearly round state after just a few hundred femtoseconds (fs). We assign these very fast structural dynamics experienced by the CO<sub>2</sub> guest to the polymer segmental motions that would be active above the glass transition temperature. In PMMA, the CLS remains high for decades of ps, demonstrating that CO<sub>2</sub> in this system experiences very few dynamics. Again, this polymer is above its glass transition temperature where many of these dynamics are deactivated. To test these conclusions, we are currently in the process of measuring the CO<sub>2</sub> dynamics in PMMA above its glass transition. We hypothesize that at this temperature the CLS will decay rapidly within a few ps, as it did in

PDMS, confirming the origin of the dynamics that are affecting the gas species.

In parallel with these polymeric systems, we have developed a sample preparation that will facilitate the CO<sub>2</sub> in MOF measurements that are crucial to the objectives of this study. This required us to introduce a hydraulic press to create low void space samples that would minimize their IR light scattering. We plan to begin measuring these samples in the next month.

## References

1. Mandal, A.; Pack, G. N.; Shah, P. P.; Erramilli, S.; Ziegler, L. D., Ultrafast Two-Dimensional Infrared Spectroscopy of a Quasifree Rotor: J Scrambling and Perfectly Anticorrelated Cross Peaks. *Phys. Rev. Lett.* **2018**, *120* (10), 6.