Investigation of the Terahertz Vibrational Modes of ZIF-8 and ZIF-90 with Terahertz Time-domain Spectroscopy

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***Abstract*— The terahertz spectra of ZIF-8 and ZIF-90 were acquired with terahertz time-domain spectroscopy (THz-TDS). *Ab initio* quantum mechanical calculations yield in spectra that match well with the experimental results and indicate that swing motions in these ZIFs may lie within the terahertz region. Variable temperature THz-TDS measurements on ZIF-90 suggest that the technique is sensitive to host-guest interactions, which can be used to study them in the future.**

I. INTRODUCTION

ZEOLITIC imidazolate frameworks (ZIFs) are a subclass of the metal-organic framework (MOF) family which have been heavily studied for applications in gas storage[1]. ZIF-8 in particular has a highly flexible molecular structure which leads to concerted 'swing' motions of the imidazole ligand,[2] and these motions have been suggested to be crucial to its adsorption properties. A recent study suggests that the terahertz frequency region is an area of great interest as *ab initio* quantum mechanical calculations predicted a number soft modes, pore breathing and gate opening motions falling in the frequency region below 3 THz[3]. However, while experimental inelastic neutron scattering spectra matched qualitatively with the simulated spectra in the crucial < 3 THz region, there was insufficient resolution of the spectral features at these frequencies to conclusively match the experimental and simulated spectra. In order to better probe the terahertz vibrational modes of these systems, terahertz time-domain spectroscopy (THz-TDS) is used to study ZIF-8 and the sister imidazolecarboxaldehyde structure, ZIF-90. New *ab initio* quantum mechanical calculations are also performed for comparison with the experimental data.

II. RESULTS

ZIF-8 and ZIF-90 were prepared using previously reported methods.[4,5] 60 mg of each ZIF sample was mixed with 360 mg of high-density polyethylene and compressed under 2 tons of force for 3 minutes to form approximately 3 mm thick pellets of 13 mm diameter for the THz-TDS measurements. Variable temperature THz-TDS measurements were performed using previously employed equipment and methodology.[6]

The terahertz spectrum of ZIF-8 at 80 K shows a weak feature at 1.51 THz, a strong feature at 1.95 THz and a feature developing at 2.5 THz (Fig. 1a); while the spectrum of ZIF-90 at 80 K shows weak features at 0.76 and 2.34 THz, and a feature developing at 2.47 THz (Fig. 1b). The simulated spectrum of ZIF-8 based on newly performed solid-state density functional theory calculations, utilizing the meta-hybrid M06-2X functional, is an excellent match to the experimental spectrum. A large number of terahertz vibrational modes are predicted for ZIF-90, and while the agreement with the experimental spectrum is not as good as that of ZIF-8, the calculations predict an observable mode below 1 THz, followed by two closely spaced modes at around 1.6 THz with similar intensities. This is the same qualitative trend observed in the experimental spectrum. Analysis of the predicted terahertz vibrational modes in both ZIF-8 and ZIF-90 shows that they mostly involve shearing and torsional motions of the imidazolate linkers. However, the strong vibrational mode predicted for ZIF-8 at 1.89 THz, as well as the vibrational modes at 1.13 and 1.31 THz predicted for ZIF-90 result from rotational motions of the linkers, which suggests that they could be the crucial swing effect motions.

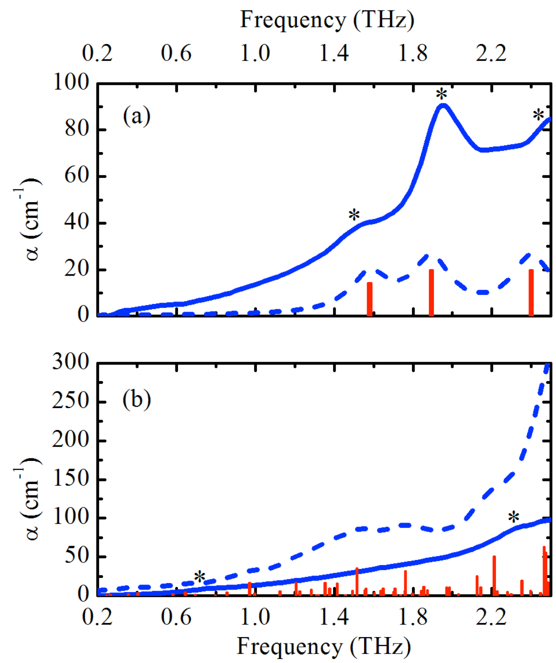

Fig. 1 Experimental and simulated terahertz spectra of (a) ZIF-8 and (b) ZIF-90. Solid lines represent experimental spectra and dashed lines represent simulated spectra. Red bars indicate frequencies and intensities of the calculated terahertz modes.

Variable temperature THz-TDS spectra showed significant differences in the 220-280 K temperature range, with a spike in absorption from 220-250 K and a decrease to the original levels from 250-280 K. This may be related to the presence of adsorbed water in ZIF-90 under ambient conditions, which initially freezes upon rapid cooling, then melts at temperatures above 220 K due to melting point depression for confined systems[7] and finally evaporates under prolonged exposure to vacuum conditions. This shows the potential of THz-TDS in future investigations of host-guest interactions in ZIFs.

In this paper, the terahertz spectrum of ZIF-8 is investigated with a combination of THz-TDS and ab initio quantum mechanical calculations. The use of THz-TDS allows for a well resolved spectrum to be obtained, while revised quantum mechanical calculations proved to be an excellent match for the experimental data. These methods were then extended to ZIF-90 and a reasonable match was also obtained between the experimental and calculated spectra. Closer analysis shows terahertz vibrational modes at 1.89 THz in ZIF-8 and 1.13 and 1.31 THz in ZIF-90, which involve rotational motions of the imidazolate linkers and hence may be the key gate-opening motions in these systems. Subsequent PXRD experiments found unusual behaviour in ZIF-90, which could be related to guest loading under ambient conditions. Variable temperature THz-TDS spectra showed significant differences in the 220–280 K temperature range. The spike in absorption and subsequent decrease to the original levels suggest the presence of adsorbed water in ZIF-90 stored under ambient conditions, which is first frozen as ice, then liquefies and subsequently vaporises.

These results demonstrate the utility of THz-TDS in the study of ZIFs and provide further evidence that the crucial gate-opening vibrations in ZIFs lie at terahertz frequencies. Furthermore, variable temperature THz-TDS is shown to be sensitive to host-guest interactions in ZIFs. This demonstrates the potential of the technique in studying such interactions in ZIFs, which will have direct applications in gas and drug loading in these systems.

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