# Impact of Pressure and Temperature on the Broadband Dielectric **Response of the HKUST-1 Metal–Organic Framework**

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**Supporting Information** 

ABSTRACT: Research on the broadband dielectric response of metal-organic frameworks (MOFs) is an emergent field that could yield exciting device applications, such as smart optoelectronics, terahertz sensors, high-speed telecommunications, and microelectronics. Hitherto, a detailed understanding of the physical mechanisms controlling the frequency-dependent dielectric and optical behavior of MOFs is lacking because a large number of studies have focused only on static dielectric constants. Herein, we employed high-resolution spectroscopic techniques in combination with periodic ab initio density functional theory (DFT) calculations to establish the different polarization processes for a porous copper-based MOF, termed HKUST-1. We used alternating current measurements to determine its dielectric response between 4 Hz and 1.5 MHz where orientational polarization is predominant, while synchrotron infrared (IR) reflectance was used to probe the far-IR, mid-IR, and near-IR dielectric response across the 1.2-150 THz range (ca. 40-5000 cm<sup>-1</sup>) where vibrational and optical



polarizations are principal contributors to its dielectric permittivity. We demonstrate the role of pressure on the evolution of broadband dielectric response, where THz vibrations reveal distinct blue and red shifts of phonon modes from structural deformation of the copper paddle-wheel and the organic linker, respectively. We also investigated the effect of temperature on dielectric constants in the MHz region pertinent to microelectronics, to study temperature-dependent dielectric losses via dissipation in an alternating electric field. The DFT calculations offer insights into the physical mechanisms responsible for dielectric transitions observed in the experiments and enable us to explain the frequency shifts phenomenon detected under pressure. Together, the experiments and theory have enabled us to glimpse into the complex dielectric response and mechanisms underpinning a prototypical MOF subject to pressure, temperature, and vast frequencies.

### INTRODUCTION

Metal-organic frameworks (MOFs) are renowned for possessing high porosity and ordered structure along with tunable physical and chemical properties. In the past few decades, the main focus of these materials was directed toward applications such as gas storage, drug delivery, and chemical separations.<sup>1-4</sup> The ability to tune the physical behavior of MOFs has opened up new avenues of research and the focus has begun to shift toward device applications, such as microelectronics, optoelectronics, luminescence and sensors.<sup>5–9</sup> For next-generation high-speed devices, an ultra "low-k" dielectric material is desirable to reduce the signal delay, power loss and electronic crosstalk with ever-shrinking device dimension and increasing number of active devices packed into an integrated circuit.<sup>10</sup> According to the International Technology Roadmap for Semiconductors

(ITRS),<sup>11</sup> the conventional materials such as SiO<sub>2</sub> whose dielectric constant, static  $\varepsilon'$  value or  $k \sim 4$ , will be replaced by a highly porous, crystalline or amorphous, chemically, and mechanically stable material in the future.<sup>12</sup> Due to the inherently low dielectric properties of MOFs, they could meet the time scale for the advancement of future low-k dielectric materials set by the ITRS.<sup>13</sup>

Hitherto only a handful of experiments have been reported on the dielectric properties of MOF materials. For example, Redel et al.<sup>14</sup> estimated the dielectric constant (k or  $\varepsilon'$ ) of HKUST-1 polycrystalline films in the visible wavelength range, assuming  $\varepsilon' = n^2$  using the value of refractive index (n)

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**Figure 1.** (a) Crystal structure of a unit cell of the HKUST-1 framework, shown here without adsorbed water molecules (color scheme: hydrogen in white, oxygen in red, copper in blue, and carbon in gray). (b) Nominal density of the pellets used for the MHz and THz measurements plotted as a function of the nominal pellet pressure. The pellets were designated in terms of the uniaxially applied force in metric tons, e.g. 0.5t for pellet pressed with a 0.5-ton force onto a 13 mm diameter die; thus, nominal stress = force/nominal area. The crystal density percentage was determined relative to the crystallographic density of HKUST-1. (c) Normalized XRD patterns of the HKUST-1 powder and pellets compressed under different loads. For comparison, the XRD patterns of pellets in absolute intensities are shown in Figure S3.

measured by spectroscopic ellipsometry. Usman et al.<sup>15</sup> synthesized a thermally stable Sr-based MOF under hydrothermal conditions and measured the dielectric response of pelletized samples using impedance spectroscopy; they suggested that the low dielectric behavior is the materials intrinsic property. Zagorodniy et al.<sup>16</sup> theoretically analyzed a series of hypothetical Zn-based MOF structures using the semiempirical Clausius-Mossotti relation and identified a number of promising candidates as ultralow k dielectrics. Such theoretical work was recently extended by Ryder et al.<sup>17</sup> for a large set of carboxylate-based frameworks. Mendiratta et al.<sup>18</sup> used an experimental and theoretical approach to study the dielectric properties of a Zn-based MOF. They calculated the polarizability using the Clausius-Mossotti relation and reported that in guest-free MOF structures the main dielectric contribution is from electronic polarization.

More recently, Scatena et al.<sup>19</sup> have reported the use of experimental and theoretical techniques to study the dielectric properties of the HKUST-1, measured up to a frequency of 1 MHz and when subjected to polar guest molecules (water and methanol). It was reported that the dielectric constant of the guest-free HKUST-1 pellet is  $\varepsilon' \sim 1.72$ , while the density functional theory (DFT) calculated value is 1.74. Distinct from other studies, some of us have characterized the frequency-dependent dielectric behavior of MIL-53(Al)<sup>20</sup> and a series of zeolitic imidazolate frameworks (ZIFs)<sup>21</sup> in the infrared regime. The broadband experiments were carried out using synchrotron specular reflectance spectroscopy, further corro-

borated by DFT calculations that accurately predicted the dynamic dielectric functions observed in the experiments. For the static dielectric constant, it has been proposed that MOFs may obey a scaling rule dominated by the framework porosity and density.<sup>17,21</sup> Despite these developments in the field of MOF dielectrics, there is no attempt yet to consider more rigorously the precise dielectric response and polarization mechanisms of MOFs when crossing the static  $\rightarrow$  kHz  $\rightarrow$  MHz  $\rightarrow$  THz frequency range. Moreover, the impact of temperature and pressure on the polarizability of MOF structures is also little understood.

In this work, we have studied the temperature- and pressuredependent broadband dielectric behavior of an activated HKUST-1 material under vacuum conditions. The MHz measurements were carried out using an LCR meter equipped with a parallel-plate capacitor arrangement operating in the frequency range of 4 Hz to 1.5 MHz, and covering the temperature range of 20 to 100 °C. The high-frequency dielectric behavior over the far-, mid-, and near-IR regions was measured via synchrotron infrared specular reflectance spectroscopy covering the range of 1.2 to 150 THz (40-5000  $cm^{-1}$ ). Details of the experimental setups are presented in the Supporting Information; see Figure S1. We performed density functional theory (DFT) calculations using the periodic CRYSTAL17 code<sup>22</sup> to gain additional insights into the effects of frequency and pressure on the broadband dielectric response of an ideal HKUST-1 structure.

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**Figure 2.** Dielectric properties of HKUST-1 as a function of temperature and pelleting pressure: (a) real part of dielectric constant  $\varepsilon'$ , (b) imaginary part of dielectric constant  $\varepsilon''$ , and (c) loss tangent, tan  $\delta = (\varepsilon''/\varepsilon')$ . The marked change in the dielectric constant of the pellets from 1t to 2t can be attributed to pellet densification and framework amorphization, supported by the steep decline in relative XRD intensity and reduction of surface roughness depicted in the inset of Figure 1b.

## RESULTS AND DISCUSSION

The as-received Basolite C300 powder (Sigma-Aldrich) also known as HKUST-1 (Figure 1a) or Cu<sub>3</sub>(BTC)<sub>2</sub> [BTC = benzene-1,3,5-tricarboxylate] was used in this study. Water molecules can readily coordinate to the apical adsorption sites of the copper paddle-wheel,<sup>23</sup> hence affecting the dielectric property of the overall framework due to the strong dipole moment of water ( $\varepsilon' \sim 80$  at 20 °C).<sup>24</sup> For this reason, in this study we have performed all dielectric measurements under vacuum conditions to activate the HKUST-1 framework, thereby eliminating the contribution of water molecules toward the total dielectric response.

We have prepared pellets of HKUST-1 with a diameter of 13 mm using a manual hydraulic press, by systematically increasing the applied force from 0.5, 1, 2, 3, 5, and 7 to 10 tons. Figure 1b shows that the prepared pellets and their nominal densities are obeying an exponential relation of the form:  $\rho \propto \exp(-\sigma)$ , where  $\rho$  is the nominal pellet density and  $\sigma$  is the nominal stress. Compared with the theoretical density of a HKUST-1 single crystal (948.9 kg m<sup>-3</sup>),<sup>23</sup> the 0.5t pellet exhibits a nominal density of ~110% while the 10t pellet attained ~195% of the theoretical density. It can be seen in Figure 1(b) that the color of the pellets is also systematically shifting from turquoise toward dark blue with the rising pressure, indicating the change of its refractive index (*vide infra*).

By increasing the pelleting pressure, one may expect a reduction of free volume between the crystals in the pellet, as evidenced from roughness characterization of the polycrystal-

line surface, see inset of Figure 1b and Figure S2. Irreversible plastic deformation of the HKUST-1 structure mimicking the trend of the density vs nominal stress curve in Figure 1b is also expected, leading to amorphization<sup>25</sup> of the porous framework. X-ray diffraction (XRD) patterns in Figure 1c and Figure S3 show the evolution of the Bragg peaks with pelleting pressure. The HKUST-1 powder starts to amorphize under stress at 37 MPa (0.5t) as evidenced by the disappearance of the (200) and (111) peaks. The (220), (222) and (400) characteristic peaks also exhibit broadening effect with increased pelleting pressure, indicating pore collapse and framework amorphization (further supported by the full width at half-maximum (fwhm) analysis in Figure S4 and Table S1). The increasing trend in fwhm values is mirroring the change of nominal density of the pellets shown in Figure 1b.

Figure 2 shows the dielectric properties of HKUST-1 with increasing pelleting pressure and temperature at the representative frequencies of 0.01, 0.1, and 1 MHz. For an individual pellet, the real part of the dielectric constant ( $\varepsilon'$ ) decreases with increasing frequency at a specific temperature. The MHz data revealed that the dipole moment of the framework cannot keep up with the alternating field switching at higher frequency, therefore resulting in an overall decline in the orientational polarizability of the material. For example, the  $\varepsilon'$  value of the 0.5t pellet at 20 °C fell from its highest value of 2.72 at 10 kHz to 2.42 at 1 MHz. For the 10t pellet, the value of  $\varepsilon'$  rose from 4.88 (20 °C) to 5.07 (80 °C) and then slightly declined to yield 4.92 at 100 °C; this effect might be linked to the negative thermal expansion of the HKUST-1 framework.<sup>26</sup>



**Figure 3.** Complex refractive index of HKUST-1, where the real part of the refractive index *n* and the imaginary part of the refractive index  $\kappa$  are plotted as a function of frequency. Panels a and c are the DFT predictions of an ideal HKUST-1 structure at zero pressure. Panels b and d show the experimental results at 20 °C for the polycrystalline samples of HKUST-1 at different pelleting pressures.

Higher pelleting pressure reduces the free volume between the crystals and increases amorphization of sample, both of which affect the dielectric response. For instance, for 1 MHz frequency at 20 °C, by increasing the pelleting pressure from 0.5t to 10t, it was found that the value of  $\varepsilon'$  can be doubled from 2.42 to 4.88. It follows that the dielectric behavior of the polycrystalline sample depends upon the pellet density; herein, our data show that it scales nonlinearly with pressure due to plastic deformation (see Figure 1b). This effect, however, is commonly neglected in the literature concerning the dielectric measurements of pelleted powder samples (e.g., refs 18 and 19). Scatena et al.<sup>19</sup> have grown HKUST-1 single crystals (~300  $\mu$ m) and prepared a pellet by employing a pressure of 200 MPa, but they did not consider the impact of structural amorphization from pelletizing process or attempt to quantify how this structural change might alter its dielectric property.

The imaginary part of the dielectric constant  $(\varepsilon'')$  is shown in Figure 2b, which represents the energy dissipation of HKUST-1 subject to an alternating electric field. We found that all pellets have a low dielectric loss of tan  $\delta < 0.075$ (Figure 2c) between 20 and 100 °C; this value declines with rising temperature, but it increases with rising frequency. For comparison, at 1 MHz, polymers such as PVDF and PMMA exhibit a small tan  $\delta$  of about 0.12<sup>27</sup> and 0.02,<sup>28</sup> respectively. It has also been reported that at 300 K a Sr-based MOF exhibits a tan  $\delta \sim 0.02$  at 0.1 MHz.<sup>15</sup> The complete pressure- and temperature-dependent dielectric data sets of the HKUST-1 pellets are presented in the Supporting Information; see Figures S8–S10.

Now we turn to the optical and dielectric properties of HKUST-1 in the broadband infrared (IR) frequencies, encompassing 40–5000 cm<sup>-1</sup>. The high-resolution reflectance spectra were measured by employing synchrotron specular reflectance spectroscopy at beamline B22 in the Diamond Light Source (Oxfordshire, U.K.); the collected reflectance spectra of HKUST-1 under different pelleting pressures are presented in Figure S11. Subsequently, the real and imaginary parts of the frequency-dependent refractive indices (Figure 3) and dielectric constants (Figure 4) were determined from the reflectance spectra by implementing the Kramers–Kronig transformation;<sup>20,29</sup> see full descriptions in the Supporting Information, section 2. To gain additional insights into the underpinning physical mechanisms, we have compared our experimental results to periodic *ab initio* DFT calculations



**Figure 4.** Complex dielectric function of HKUST-1 over the broadband frequency range of 4 Hz to 150 THz. (a, b) Real part of the dielectric constant  $\varepsilon'$  and (e, f) imaginary part of the dielectric constant  $\varepsilon''$ , calculated by DFT for an ideal HKUST-1 structure at zero pressure. The IR intensities are mainly related to the transition dipole moment, for instance the most intense IR peak at 1408 cm<sup>-1</sup> corresponds to the symmetric stretching of the carboxylate group. (c, d) Real part and (g, h) imaginary part of dielectric constants determined from experiments for pelletized HKUST-1 samples prepared under different forces. For the experimental data, the left panels show the Hz-MHz range measured by LCR parallel-plate capacitor technique, while the right panels show the far-IR, mid-IR, and near-IR regions measured by synchrotron specular reflectance spectroscopy. Note that the synchrotron measurements (i) were limited to the 0.5t, 1t, 2t, 5t, and 10t pellets only, and (ii) the drop off in intensity below ~3 THz is an artifact due to frequency cutoff by the far-IR beamsplitter.

carried out with the hybrid B3LYP-D3(ABC) functional incorporating two- and three-body dispersion forces,<sup>30</sup> combined with a triple-zeta quality basis set (see computational methods in the Supporting Information, section 10).

First, we consider the broadband optical properties of HKUST-1 as a function of frequency ( $\omega$ ) and pelleting pressure. Figure 3 shows the real (n) and imaginary ( $\kappa$ ) parts of the complex refractive index  $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$ , plotted against the DFT predictions showing the general agreement between experiments and theory across the wide frequency range. The experimental spectra show that the value of n varies from 1.15 to 1.2 for all the pellets in the NIR region (>100 THz), which is reminiscent of the value of n = 1.34 calculated by DFT for the ideal HKUST-1 structure. The refractive indices increase as a function of pelleting pressure due to the increment in nominal pellet density (Figure 1b) and mechanically induced amorphization (Figure 1c), which togeth-

er will result in reduction of free volume  $(n \sim 1)$  within a polycrystalline sample. For a particular pelleting pressure, we note the following: (a) The refractive index experiences a stepwise decrease with increasing frequency, the mechanisms of which will be addressed in the sections below. (b) At each transition step, there is a discontinuity in the real part of the refractive index *n*, because of dissipative losses, giving rise to absorption peaks within the imaginary part of the refractive index  $\kappa$ .

Figure 4 presents the combined broadband dielectric spectra (theory vs experiments) starting from 4 Hz up to 150 THz, to enable us to establish a complete understanding of the frequency- and pressure-dependent dielectric response of the HKUST-1 framework. To maintain consistency in the data, the broadband spectra only displays the pellet data collected at 20 °C. The complex dielectric function is  $\tilde{\epsilon}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ , which comprises the real and imaginary components denoted

Table 1. Contributions of the Main Polarization	Mechanisms to the	Total Dielectric Res	ponse of HKUST-1 <sup>a</sup>
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	polarization mechanisms						
	${oldsymbol{arepsilon}}'_{ ext{dipole/orientational polarization}}$	${m {m {arepsilon}}}'_{ m atomic/vibrational}$ polarization		${m {arepsilon}}'_{ m optical/electronic \ polarization}$	${oldsymbol{arepsilon'}}_{ ext{total}}$		
pelleting pressure/MPa	MHz (4 Hz to 1.5 MHz)	far-IR (1.5–20 THz)	mid-IR (20-100 THz)	near-IR (100–150 THz)	entire spectrum		
$0 (DFT)^{b}$	0	0.12	0.18	1.49	1.79		
36.96 (0.5t)	1.32	0.15	0.14	1.36	2.97		
73.92 (1t)	1.33	0.2	0.17	1.48	3.18		
147.84 (2t)	2.05	0.39	0.26	1.55	4.25		
369.60 (5t)	2.03	0.77	0.32	1.30	4.42		
739.20 (10t)	3.17	0.71	0.44	1.44	5.76		

<sup>*a*</sup>The contribution of space charge is not considered in this analysis. <sup>*b*</sup>O MPa data obtained from DFT calculations of an ideal HKUST-1 structure. We observed that the theoretical value (1.79) is reminiscent of experimental values of the 0.5t and 1t pellets upon removal of their dipolar contributions ( $\varepsilon'_{\text{total}} - \varepsilon'_{\text{dipole}}$ ), resulting in values that lie in the range of 1.65 to 1.85.

by  $\varepsilon'$  and  $\varepsilon''$ , respectively. It is evident from the broadband spectral data that the dielectric value decreases with increasing frequency and the static dielectric constant  $\varepsilon'$  ( $\omega = 0$ ) denotes the maximum value of HKUST-1.

In the near-IR region (100–150 THz), the dielectric spectra of the HKUST-1 pellets show an asymptotic behavior where  $\varepsilon'$  values were found to be lying in a narrow band of 1.3–1.5 (see inset of Figure 4d). This is in good agreement with the DFT values of ~1.5 beyond 100 THz. Because the dielectric mechanism in the near-IR region is attributed to femtosecond  $(10^{-15} \text{ s})$  response of the electron density,<sup>31</sup> the dielectric constants at high frequencies are exclusively optical dielectric responses that are not sensitive to the structural deformation of HKUST-1 or the pelleting pressure used.

Descending the frequency scale, we arrive at the mid-IR (~10-100 THz) region; here, the dielectric mechanism is controlled by polarization processes ascribed to a subpicosecond response time of  $10^{-14} - 10^{-13}$  s, especially atomic oscillations like bending, stretching, and torsional modes of molecular moieties. However, in the far-IR region, <10 THz, the dielectric constants are controlled by the picosecond  $(10^{-12} \text{ s})$  response of collective atomic vibrations or phonon modes, where the polarizability depends on the polarity of the chemical bonds in the framework and amplitude of the vibrations. From the theoretical DFT spectra of the ideal HKUST-1 structure, it can be seen that the resonance positions of  $\varepsilon'$  (Figure 4b) and the corresponding absorption peaks of  $\varepsilon''$  (Figure 4f) below 50 THz are in good agreement with the experimental spectra; also see the superimposed spectra in Figures S12 and S13. Indeed the distinctive transitions identified in the far-IR region originated from THz lattice dynamics prevalent in the HKUST-1 framework; for exemplar, the copper paddle-wheel vibrational motions and the BTC linker deformations at ~9 THz and ~16 THz, respectively.<sup>32</sup> (For description of other THz modes in HKUST-1, the reader should refer to ref 32.) Thus, in the mid- and far-IR regions, the dielectric function is strongly affected by the dynamics of the framework structure and the pellet density, as evidenced from synchrotron data shown in parts d and h of Figure 4, whereby the values of  $\varepsilon'$  and  $\varepsilon''$ systematically increased with pelleting pressure.

In the MHz frequency region, the polarization process is considerably slower with a microsecond  $(10^{-6} \text{ s})$  response time. The dielectric response in this region could originate from the dipole polarization of the framework surrounding the Cu(II) paddle-wheel sites.<sup>19,33</sup> We reasoned that this process is enhanced by the structural distortion of the framework, resulting in increased of net dipole moments from plastic

deformation. This notion is supported by data in parts c and g of Figure 4, showing that the dielectric constant in the MHz range scales with pellet densification; for instance the value of  $\varepsilon'$  has doubled from ~ 2.4 to 4.9 (at 1 MHz) when the pelleting pressure was raised from 0.5t to 10t. An additional contribution is from the orientational polarization of dipolar species, such as residual DMF solvents (see Supporting Information, section 5) remained trapped in HKUST-1 after sample evacuation.

Finally, we note that the value of static dielectric constant from DFT calculations for an ideal HKUST-1 structure is 1.79, see Figure 4a, which resembles the previously computed values reported in literature via DFT methods ( $\varepsilon' = 1.6$ ,<sup>17</sup> 1.74)<sup>19</sup> or by using the semiempirical Clausius–Mossotti relation ( $\varepsilon'$  = 1.7).<sup>16</sup> In contrast, from the experimental data in Figure 4c, we found the dielectric constant value for the 0.5t pellet to be relatively higher at  $\varepsilon' \sim 3$  (at 100 Hz). This discrepancy might be attributed to two factors. (i) Framework amorphization and pellet densification will reduce the overall free volume ( $\varepsilon' \sim 1$ ) in sample. (ii) DFT did not account for orientational (dipolar) polarization contribution caused by framework deformation, also the ideal HKUST-1 structure is free from all guest molecules. Note that the Clausius-Mossotti relation neglects both orientational and vibrational polarizations; consequently, the theoretical models underestimate the dielectric permittivity. In addition, thermal effects could also play a role, but in this case, the very small negative thermal expansion<sup>26</sup> of HKUST-1 leads to a tiny contraction of the unit cell when increasing temperature without significant change of the framework. From DFT calculations, it has been estimated that the increment of the dielectric constant is of the order of 10<sup>-3</sup>.

It follows that the broadband dielectric data gathered experimentally and theoretically have enabled us to further breakdown the individual contributions, into the three main polarization mechanisms. The results for HKUST-1 are summarized in Table 1, where the total dielectric permittivity is taken as  $\varepsilon'_{\text{total}} = \varepsilon'_{\text{dipole/orientational}} + \varepsilon'_{\text{atomic/vibrational}} + \varepsilon'_{\text{optical/electronic}}$ 

Figure 5a summarizes the changing trend of  $\varepsilon'$  with frequency, clearly demonstrating that there exists a strong sensitivity toward the mechanically induced structural deformation of HKUST-1 in the frequency region of below 50 THz. We note that the increase of dielectric values when progressing from the mid-IR to the far-IR region is significantly greater than those recorded through the near-IR range. Likewise, in the Hz-MHz range there is a clear dependency on mechanical stress applied during pelleting, as shown in



**Figure 5.** (a) Summary of the dielectric constants of HKUST-1 across the broadband frequencies comprising the far-, mid-, and near-IR regions. (b) Blue and red shifts of the THz peaks linked to the copper paddle-wheel and BTC linker vibrational modes plotted as a function of pelleting pressure; the inset shows the corresponding DFT predictions under hydrostatic pressure.

Figure 6a. To gain further insights, we investigated the effect of mechanical deformation on the dielectric and optical properties of HKUST-1 using DFT calculations, which was achieved by imposing a hydrostatic pressure of 0, 190, and 360 MPa onto a cubic unit cell of HKUST-1; the results are shown in Figure 6b. While the cell volume declines with pressure as expected, we found that from 190 to 360 MPa the unit cell underwent a cubic to tetragonal transformation indicating mechanical instability triggered by a threshold pressure beyond ~190 MPa. In fact, we recognize that the nature of loading under nominal stress (experienced by pellets) is not identical to the hydrostatic pressure simulated by DFT, but the theoretical results shed light on the scope of employing mechanical deformation for tuning the dielectric response of a porous framework.

As the HKUST-1 framework is mechanically deformed by pellet formation, see Figure 1b (even at the lowest force of 0.5t), we discovered that the applied stress has resulted in THz peak shifts. Two interesting examples are shown in Figure 5b, where the magnitude of peak shifts is plotted as a function of nominal stress. The vibrational modes at  $\sim$ 8 and  $\sim$ 14 THz are associated with the collective dynamics of the copper paddle-



**Figure 6.** Effects of nominal stress or pressure on the dielectric constants of HKUST-1. (a) Experimental values of  $\varepsilon'$  obtained from the pelletized sample measured at kHz-MHz frequencies. The curves are guides for the eye. (b) Static dielectric values computed by DFT for  $\varepsilon'$  and  $\varepsilon''$  at 0, 190, and 360 MPa. Inset shows the predicted change of the primitive cell volume with applied pressure, where volumetric strain is defined as  $\Delta = \frac{\Delta V}{V_0} \times 100\%$ . In turn, polarizability was predicted to decline with pressure, which is not unexpected because polarizability is usually proportional to the unit cell volume.

wheel (metal clusters) and the phonon modes of the BTC linkers, respectively.<sup>32</sup> THz vibrations of the copper paddlewheel exhibits a blueshift with increasing stress/pressure corresponding to stiffening of the cluster deformation modes also predicted by DFT. Notably, there is a steep rise in the first  $\sim 200$  MPa that can be linked to plastic deformation of the framework. On the other hand, phonon modes of the BTC linkers are softening with stress/pressure, because redshifts were detected with an increasing mechanical loading. It is quite fascinating that the simulated and experimental spectra are demonstrating a similar trend (against DFT results in Figure 5 inset), except for the peak broadness of experimental data that can be attributed to polycrystalline nature of the pelletized samples. This peak broadening is more evident in the far-IR region because the pelleting stress will have a higher impact on the collective lattice dynamics of the framework, as compared to the mid-IR region dictated by vibrational modes of the local chemical moieties.<sup>34</sup> In the near-IR region, we note that there is some pressure dependence between ca. 55 and 110 THz because of a continuous increase in electronic polarization as a

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function of structural deformation generated by the pelleting stress. Complete analysis of the individual peak shifts in the dielectric and refractive index spectra is presented in Figures S15–S18 of the Supporting Information. Finally, the loss tangent spectra of pellets across the broadband frequencies are shown in Figure S14, demonstrating the substantially greater dissipation detected in the THz region (relative to the MHz losses) due to collective lattice dynamics and phonon vibrations of the HKUST-1 framework.

## CONCLUSIONS

In conclusion, we reported pressure- and temperaturedependent broadband dielectric response for HKUST-1 covering the vast frequency region of 4 Hz to 150 THz. This study was made possible by employing a combination of experimental and theoretical methods. The main findings are summarized as follows:

- Dielectric constants of HKUST-1 can be modified through the application of pelleting pressure and temperature, indicating its dependency on the structural deformation, sample amorphization, and densification which are associated with the free volume and framework polarizability.
- The dielectric (and optical) response of HKUST-1 in the MHz, far-IR, and mid-IR regions scales very strongly with the sample microstructure, but it is independent of the framework structure within the near-IR region.
- Multiple dielectric mechanisms and polarization processes are present in HKUST-1 that can be triggered using different frequencies, namely the following: (i) Microsecond response in MHz region-dipole polarization of the framework and orientational polarization of guest molecules. (ii) Picosecond response in far-IR-soft modes and THz collective dynamics of flexible framework. (iii) Subpicosecond response in mid-IR-atomic oscillations of molecular moieties of the framework. (iv) Femtosecond response from electronic polarization in near-IR-optical dielectric response, which is also sensitive to the structural densification of the HKUST-1 framework.
- In the far- and mid-IR regions, the degree of redshift or blueshift experienced by the vibrational modes controlling the optical and dielectric response is tunable by mechanical deformation imposed by an externally applied stress/pressure. This result is confirmed by pressure-dependent DFT calculations of an ideal HKUST-1 structure.
- The dielectric values of evacuated MOF materials can be appreciably lower than conventional dielectrics (e.g.,  $SiO_{2^{j}} \varepsilon' \sim 4$ ), they could function as a tunable dielectric for development into high-frequency applications targeting photonic sensors and THz communication devices.
- This study also led us to identifying key challenges that could hinder the use of MOFs for engineering ultra lowk dielectrics: (i) Complete activation of MOFs is not trivial, to eliminate trapped solvents effecting dipole polarizations at low frequencies. (ii) Porous MOF is susceptible to amorphization and structural deformation subject to thermo-mechanical stresses. (iii) MOF powders are difficult to shape for device integration.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b08125.

Materials characterization, TGA and FTIR analyses, pellets surface topography, reflectivity spectra, MHz and THz dielectric data, methods for DFT calculations, and detailed analyses of pressure-dependent DFT data (PDF)

CRYSTAL input files for the ideal HKUST-1 structure for both the high and low symmetry phases (ZIP)

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# **Author Contributions**

J.-C.T. conceived the project. A.S.B. performed the MHz experiments and analyzed the dielectric data with input from J.-C.T. L.D. and B.C. performed the DFT calculations and theoretical analysis. M.R.R., K.T., A.K.C., and Z.Z. performed the THz synchrotron experiments with guidance from M.D.F. and C.S.K., and under the supervision of G.C.. A.S.B. analyzed the synchrotron data with input from K.T. and J.C.T. A.S.B. and J.-C.T. wrote the manuscript with input from all coauthors.

# Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Gao, C. Y.; Tian, H. R.; Ai, J.; Li, L. J.; Dang, S.; Lan, Y. Q.; Sun, Z. M. A microporous Cu-MOF with optimized open metal sites and pore spaces for high gas storage and active chemical fixation of CO<sub>2</sub>. *Chem. Commun.* **2016**, *52*, 11147–11150.

(2) Tchalala, M. R.; Bhatt, P. M.; Chappanda, K. N.; Tavares, S. R.; Adil, K.; Belmabkhout, Y.; Shkurenko, A.; Cadiau, A.; Heymans, N.; De Weireld, G.; Maurin, G.; Salama, K. N.; Eddaoudi, M. Fluorinated MOF platform for selective removal and sensing of SO<sub>2</sub> from flue gas and air. *Nat. Commun.* **2019**, *10*, 1328.

(3) McKinlay, A. C.; Allan, P. K.; Renouf, C. L.; Duncan, M. J.; Wheatley, P. S.; Warrender, S. J.; Dawson, D.; Ashbrook, S. E.; Gil, B.;

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Marszalek, B.; Düren, T.; Williams, J. J.; Charrier, C.; Mercer, D. K.; Teat, S. J.; Morris, R. E. Multirate delivery of multiple therapeutic agents from metal-organic frameworks. *APL Mater.* **2014**, *2*, 124108.

(4) Belmabkhout, Y.; Zhang, Z. Q.; Adil, K.; Bhatt, P. M.; Cadiau, A.; Solovyeva, V.; Xing, H. B.; Eddaoudi, M. Hydrocarbon recovery using ultra-microporous fluorinated MOF platform with and without uncoordinated metal sites: I- structure properties relationships for  $C_2H_2/C_2H_4$  and  $CO_2/C_2H_2$  separation. *Chem. Eng. J.* **2019**, 359, 32–36.

(5) Stassen, I.; Burtch, N.; Talin, A.; Falcaro, P.; Allendorf, M.; Ameloot, R. An updated roadmap for the integration of metal-organic frameworks with electronic devices and chemical sensors. *Chem. Soc. Rev.* 2017, *46*, 3185–3241.

(6) Chaudhari, A. K.; Kim, H. J.; Han, I.; Tan, J. C. Optochemically responsive 2D nanosheets of a 3D metal-organic framework material. *Adv. Mater.* **2017**, *29*, 1701463.

(7) Dolgopolova, E. A.; Shustova, N. B. Metal–organic framework photophysics: Optoelectronic devices, photoswitches, sensors, and photocatalysts. *MRS Bull.* **2016**, *41*, 890–896.

(8) Chaudhari, A. K.; Souza, B. E.; Tan, J.-C. Electrochromic thin films of Zn-based MOF-74 nanocrystals facilely grown on flexible conducting substrates at room temperature. *APL Mater.* **2019**, *7*, No. 081101.

(9) Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Metal-organic frameworks: functional luminescent and photonic materials for sensing applications. *Chem. Soc. Rev.* **2017**, *46*, 3242–3285.

(10) Volksen, W.; Miller, R. D.; Dubois, G. Low Dielectric Constant Materials. *Chem. Rev.* **2010**, *110*, 56–110.

(11) Hoefflinger, B. ITRS: The International Technology Roadmap for Semiconductors. *Chips* 2020 **2011**, 161–174.

(12) Maex, K.; Baklanov, M. R.; Shamiryan, D.; lacopi, F.; Brongersma, S. H.; Yanovitskaya, Z. S. Low dielectric constant materials for microelectronics. *J. Appl. Phys.* **2003**, *93*, 8793.

(13) Usman, M.; Lu, K.-L. Metal–organic frameworks: The future of low-κ materials. *NPG Asia Mater.* **2016**, *8*, e333.

(14) Redel, E.; Wang, Z.; Walheim, S.; Liu, J.; Gliemann, H.; Woell, C. On the dielectric and optical properties of surface-anchored metalorganic frameworks: A study on epitaxially grown thin films. *Appl. Phys. Lett.* **2013**, *103*, No. 091903.

(15) Usman, M.; Lee, C.-H.; Hung, D.-S.; Lee, S.-F.; Wang, C.-C.; Luo, T.-T.; Zhao, L.; Wu, M.-K.; Lu, K.-L. Intrinsic low dielectric behaviour of a highly thermally stable Sr-based metal–organic framework for interlayer dielectric materials. *J. Mater. Chem.* C 2014, 2, 3762–3768.

(16) Zagorodniy, K.; Seifert, G.; Hermann, H. Metal-organic frameworks as promising candidates for future ultralow-*k* dielectrics. *Appl. Phys. Lett.* **2010**, *97*, 251905.

(17) Ryder, M. R.; Donà, L.; Vitillo, J. G.; Civalleri, B. Understanding and controlling the dielectric response of metalorganic frameworks. *ChemPlusChem* **2018**, *83*, 308–316.

(18) Mendiratta, S.; Usman, M.; Chang, C.-C.; Lee, Y.-C.; Chen, J.-W.; Wu, M.-K.; Lin, Y.-C.; Hsu, C.-P.; Lu, K.-L. Zn(II)-based metal– organic framework: an exceptionally thermally stable, guest-free low dielectric material. *J. Mater. Chem. C* **2017**, *5*, 1508–1513.

(19) Scatena, R.; Guntern, Y. T.; Macchi, P. Electron density and dielectric properties of highly porous MOFs: binding and mobility of guest molecules in  $Cu_3(BTC)_2$  and  $Zn_3(BTC)_2$ . J. Am. Chem. Soc. **2019**, 141, 9382.

(20) Titov, K.; Zeng, Z.; Ryder, M. R.; Chaudhari, A. K.; Civalleri, B.; Kelley, C. S.; Frogley, M. D.; Cinque, G.; Tan, J. C. Probing dielectric properties of metal-organic frameworks: MIL-53(Al) as a model system for theoretical predictions and experimental measurements via synchrotron far- and mid-infrared spectroscopy. *J. Phys. Chem. Lett.* **2017**, *8*, 5035–5040.

(21) Ryder, M. R.; Zeng, Z.; Titov, K.; Sun, Y.; Mahdi, E. M.; Flyagina, I.; Bennett, T. D.; Civalleri, B.; Kelley, C. S.; Frogley, M. D.; Cinque, G.; Tan, J. C. Dielectric properties of zeolitic imidazolate frameworks in the broad-band infrared regime. J. Phys. Chem. Lett. 2018, 9, 2678-2684.

(22) Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C. M.; Civalleri, B.; Maschio, L.; Rerat, M.; Casassa, S.; Baima, J.; Salustro, S.; Kirtman, B. Quantum-mechanical condensed matter simulations with CRYSTAL. *WIREs Comput. Mol. Sci.* **2018**, *8*, e1360.

(23) Chui, S. S.; Lo, S. M.; Charmant, J. P.; Orpen, A. G.; Williams, I. D. A chemically functionalizable nanoporous material  $[Cu_3(TMA)_2(H_2O)_3]_n$ . Science 1999, 283, 1148–50.

(24) Malmberg, C. G.; Maryott, A. A. Dielectric constant of water from  $0^{\circ}$  to 100 °C. J. Res. Natl. Bur. Stand. **1956**, 56, 1–8.

(25) Bennett, T. D.; Goodwin, A. L.; Dove, M. T.; Keen, D. A.; Tucker, M. G.; Barney, E. R.; Soper, A. K.; Bithell, E. G.; Tan, J. C.; Cheetham, A. K. Structure and properties of an amorphous metalorganic framework. *Phys. Rev. Lett.* **2010**, *104*, 115503.

(26) Wu, Y.; Kobayashi, A.; Halder, G. J.; Peterson, V. K.; Chapman, K. W.; Lock, N.; Southon, P. D.; Kepert, C. J. Negative thermal expansion in the metal-organic framework material  $Cu_3(1,3,5)$ -benzenetricarboxylate)<sub>2</sub>. Angew. Chem., Int. Ed. **2008**, 47, 8929–8932.

(27) Song, Y.; Shen, Y.; Hu, P.; Lin, Y.; Li, M.; Nan, C. W. Significant enhancement in energy density of polymer composites induced by dopamine-modified  $Ba_{0.6}Sr_{0.4}TiO_3$  nanofibers. *Appl. Phys. Lett.* **2012**, *101*, 152904.

(28) Tamboli, M. S.; Palei, P. K.; Patil, S. S.; Kulkarni, M. V.; Maldar, N. N.; Kale, B. B. Polymethyl methacrylate (PMMA)-bismuth ferrite (BFO) nanocomposite: low loss and high dielectric constant materials with perceptible magnetic properties. *Dalton Trans.* **2014**, 43, 13232–13241.

(29) Roessler, D. M. Kramers-Kronig analysis of reflection data. *Br. J. Appl. Phys.* **1965**, *16*, 1119–1123.

(30) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(31) Wilson, J. N.; Frost, J. M.; Wallace, S. K.; Walsh, A. Dielectric and ferroic properties of metal halide perovskites. *APL Mater.* **2019**, *7*, No. 010901.

(32) Ryder, M. R.; Civalleri, B.; Cinque, G.; Tan, J. C. Discovering connections between terahertz vibrations and elasticity underpinning the collective dynamics of the HKUST-1 metal–organic framework. *CrystEngComm* **2016**, *18*, 4303–4312.

(33) Lin, K.-S.; Adhikari, A. K.; Ku, C.-N.; Chiang, C.-L.; Kuo, H. Synthesis and characterization of porous HKUST-1 metal organic frameworks for hydrogen storage. *Int. J. Hydrogen Energy* **2012**, *37*, 13865–13871.

(34) Ryder, M. R.; Civalleri, B.; Bennett, T. D.; Henke, S.; Rudić, S.; Cinque, G.; Fernandez-Alonso, F.; Tan, J. C. Identifying the Role of Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization. *Phys. Rev. Lett.* **2014**, *113*, 215502.