Terahertz spectroscopy of MOFs reveals dynamic structure and contact free ultrafast photoconductivity ⓕ

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ABSTRACT

Metal-organic frameworks (MOFs) are porous crystalline materials. Their large pores make them particularly interesting for membranes, gas separation, and gas storage. Furthermore, MOFs are ultralight, making them suitable for a large realm of exciting applications ranging from wearable devices to space technology. Optimizing MOFs for these applications demands a detailed understanding of their low energy dynamics and photophysics, which can be provided by terahertz (THz) spectroscopy. MOFs exhibit structural modes, or phonons, with energies in the meV range, which corresponds to the THz spectral range (0.1–10 THz, 0.4–40 meV). Understanding these modes is crucial in determining how a MOF interacts with guest molecules in the process of gas capture and storage. In this perspective, we discuss how gas–MOF interactions alter the MOFs' spectral fingerprints. We demonstrate that THz spectroscopy can be used for gas adsorption monitoring and explain how density functional theory, together with THz spectra, can illuminate the dynamic structure of MOFs, providing unique insight into their functionality. THz is also a contact free probe for conductivity and allows us to measure short range conductivity within an individual MOF crystal. We will discuss the advantages of THz as a conductivity probe for MOFs as compared to more established direct current techniques. We will then expand our view to incorporate ultrafast photoconductivity in MOFs measured via optical pump-THz probe spectroscopy, in comparison to more established ultrafast spectroscopic tools such as optical transient absorption and photoluminescence. We will supplement this section with a discussion of THz studies on perovskites, which unveiled electron–phonon interactions not yet explored in MOFs.

I. INTRODUCTION

Metal organic frameworks (MOFs) are highly ordered, porous, and tunable materials, making them versatile for use in a variety of applications.[1] MOFs are structured as repeating units of inorganic (metallic) nodes connected by organic linkers, called ligands.[2] One of the primary attributes of MOFs is their diverse topology, often inspired by natural minerals.[3] The preparation of MOFs through reticular synthesis allows for their organic and inorganic constituents to be varied with outstanding flexibility. This flexibility is partially responsible for the exponential rise of the field,[4] resulting in a wide variety of MOFs with different pore sizes, geometries, and electro-chemical compositions, all designed with specific

functionality in mind.[5] The second driver of growth in the MOF field is that most MOFs are synthesized from earth-abundant materials and are associated with a general ease of fabrication. As a result, MOFs typically have low production costs and have demonstrated their potential for reaching competitive pricing for large scale applications.[6] Given their unique characteristics, MOFs have quickly come to prominence in materials science.[1]

The electrical properties of condensed matter are defined by electron–orbital energies and overlap. In the case of rigid, closely packed solids, the orbital overlap between periodic, identical building blocks gives rise to a band structure in which electrons are delocalized. Such close packing is rather rare in porous frameworks, which are associated with a large distance between building blocks.

In addition, the energy levels within the ligands are typically not aligned with those of the metal nodes, resulting in insulating materials.[7] Insulating MOFs have proven useful for a variety of applications, including gas separation, storage, and drug delivery.[4] Their high porosity and adjustable pore size make MOFs ideally suited for these applications. We will discuss the characterization of insulating MOFs designed for gas separation and storage applications using terahertz (THz) spectroscopic techniques in Sec. IV.

A few MOFs can be designed to enable orbital overlap and long-range charge mobility. These materials are particularly exciting as they merge the porosity of MOFs with electrical conductivity. Their electrical conductivity has been leveraged to design electrical read out gas sensors,[8] supercapacitors,[9] electrocatalysts,[10] and more. Even in these conductive MOFs, the overlap is weaker than in classically closely packed solids. As such, the term "band" needs to be critically assessed in relation to the energy levels of these materials. These energy levels can be labeled in the solid state physics picture using valence and conduction band terminology[2] or with a focus on the molecular nature using the highest occupied and lowest unoccupied molecular orbital (HOMO/LUMO) terminology. The localization of electrons in a HOMO/LUMO would allow only hopping-type charge transport.[7] Both terms will henceforth be used interchangeably, despite the fact that some MOFs will be more bandlike in structure than others.

The targeted design of MOFs for specific applications usually starts by selecting building blocks with the desired physical and chemical properties. Conductive MOFs are generally designed to accommodate one of the charge transport pathways shown in Fig. 1. The through-bond pathway represented in Fig. 1(a) consists of both metal and ligand functional group components, while the through-space pathway consists of stacked organic components that exhibit $\pi-\pi$ interactions with each other.[11]

Despite these targeted design considerations, the whole is more than the sum of its parts, and to really understand and predict the properties of a final MOF, the assembled material needs to be investigated carefully. Only if we understand the physics governing their behavior can we improve existing MOFs and predict the performance of new ones. This understanding can be achieved with a combination of complementary spectroscopic techniques.

Fourier transform infrared (FTIR) spectroscopy, optical transient absorption (OTA), and x-ray diffraction (XRD) are techniques commonly used to explore novel materials.[12] Complementary to these more established techniques, THz spectroscopy can be used to provide an enhanced understanding of a MOF's conductivity, photophysics, dynamic structure, and MOF-guest interaction. The physical phenomena that manifest in the terahertz range include high-frequency conductivity related to free charges, dielectric effects, and resonances from bound charges (including phonons).[13,14] This insight into conductivity and dynamic structure makes THz spectroscopy a powerful tool in guiding the quest to improve the efficiency of MOFs in various applications. Figure 2 illustrates the trend in the number of studies exploring THz dynamics in MOFs, highlighting a notable increase starting in 2017.

This perspective highlights the insight gained from THz spectroscopy of MOFs and how this can be leveraged to improve a MOF's conductivity or its ability to capture and store gases. We will compare THz spectroscopy to more established techniques, namely XRD, OTA, and FTIR, highlighting the complementary nature of THz spectroscopy and the additional insight we can gain from utilizing THz to better understand MOFs (Sec. II). We will then discuss MOFs in the context of solar applications (Sec. III). We will discuss THz photoconductivity measurements and provide an outlook
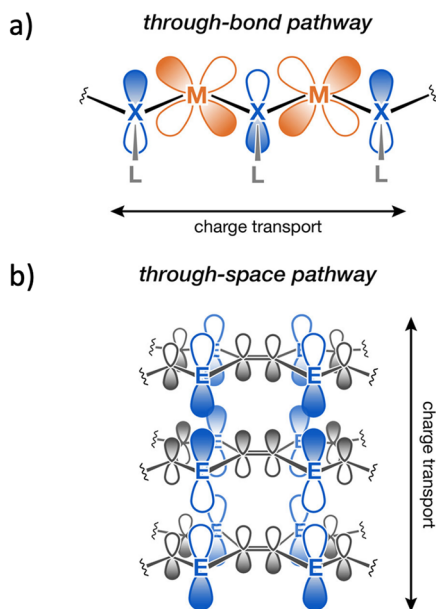

FIG. 1. Representative charge transport pathways in conductive MOFs. (a) Through-bond pathway involving metal and ligand orbitals. (b) Through-space pathway involving stacked organic components. Adapted from Xie et al., Chem. Rev. 120, 8536–8580 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution 4.0 License.
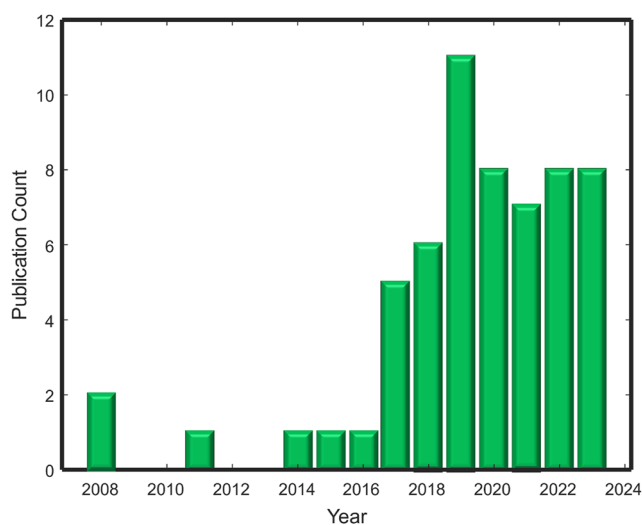

FIG. 2. The number of publications relating to THz studies on MOFs per year. The field has grown in popularity since 2017. In 2019, the first measurements of THz photoconductivity in MOFs opened up another exciting field for further investigation.

toward exciton dynamics, illustrated for perovskite examples but not yet measured in MOFs to date. This perspective will close with a discussion of THz modes and interactions in gas capture, separation, and storage processes (Sec. IV). We will emphasize what we can learn from THz modes and how this knowledge can guide future research into more targeted and exciting studies on MOFs.

II. THz COMPARED TO OTHER TECHNIQUES

This perspective does not encompass the details of terahertz spectroscopic techniques. This topic was covered in detail in several books and recent tutorials, and we kindly refer the reader to these in-depth publications for THz spectroscopy in general.[13,15–17] We will limit our discussions here to the exciting results and properties measured with THz spectroscopy and strive to provide sufficient background information to understand and appreciate these exciting investigations.

In this section, we discuss THz spectroscopy as it compares to more established characterization techniques. As illustrated in Fig. 3, each of these techniques probes different physical phenomena in a material, and, as such, provides different insights into the material's properties.

X-ray diffraction (XRD) is an established technique used to measure the static crystal lattice. XRD systems are commercially available and easy to use. XRD is a crucial first step to verify that the synthesis yielded the intended crystalline material, as it provides information such as sample purity, crystallite size, and phase identity.[18] These properties provide a static snapshot of the crystal, while THz time-domain spectroscopy (THz-TDS) provides information about the dynamic lattice.[19] Analysis of the dynamic lattice is more important for guest–host interaction, which is particularly relevant when discussing gas storage in MOFs. THz-TDS provides information about the phonon modes populated at room temperature. In conjunction with the static picture and density functional theory (DFT) or MD calculations, a detailed understanding of guest–host interaction can be achieved.[20]
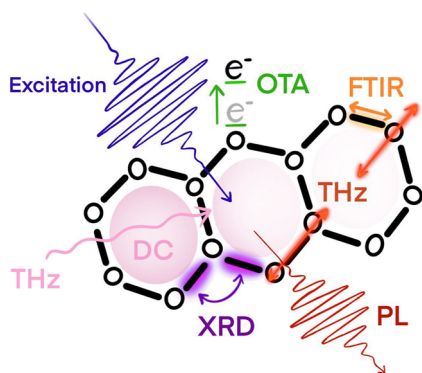

FIG. 3. Comparison of various techniques used to characterize MOFs. Direct current (DC) measurements can be used to understand long range conductivity, while THz measures conductivity on a microscopic scale. XRD provides insight into crystal structure, FTIR into local binding, and THz spectroscopy can measure the dynamic structure, complementing both techniques. Finally, optical transient absorption (OTA) and photoluminescence (PL) probe excited state dynamics, which can be complemented with ultrafast THz photoconductivity measurements.

THz spectroscopy detects the long-range, low energy (2–30 meV) dynamic modes in a MOF. More common techniques, such as IR spectroscopy, explore vibrational modes in the range above 100 meV. In particular, Fourier transform infrared (FTIR) spectroscopy can be used to identify bonding motifs by measuring changes in bond lengths and bond angles.[21] These short-range interactions provide a local picture of the chemical binding between a few atoms. This insight is crucial to understand how these MOFs are assembled, but the dynamic structure is only detectable in the lower energy range. Hence, THz-TDS is more sensitive to structural changes caused by chirality and is more effective at measuring bulk motions as opposed to localized vibrations.[22]

Photovoltaics, ultra-light electronics, and electrical read-out sensors all require a detailed understanding of the direct current properties of the utilized materials. The simplest choice to determine conductivity is two probe direct current (DC) measurements. These measurements require the fabrication of electrical contacts, which is not only time consuming, but can also change the properties of the material being studied. Furthermore, DC-measurements only probe long-range conductivity. In terms of solar applications, these DC conductivity measurements are more representative of the conductivity within a fully formed solar cell. However, in solar materials research, the full cell assembly is the last step, and understanding the materials as synthesized is a crucial early step to determine whether a specific material is worth investing the time and resources needed for large scale layer deposition. THz measurements are ideally suited to achieve this task.

Terahertz spectroscopy measures conductivity on the nanoscale with sub-picosecond resolution and does not require the fabrication of electrical contacts, making it an excellent choice for analyzing raw materials. THz measurements provide a spectrally resolved, complex-valued conductivity over a broad spectral band (0.3–5 THz). Complex conductivity describes not only the ohmic losses but also phase delays in the induced current. These conductivity spectra provide insight into scattering mechanisms and the physics that limit conductivity. In particular, THz spectroscopy can separate inter-grain and intra-grain resistance and determine whether interfaces or bulk resistance limit the conductivity.[23] If the bulk conductivity is limiting, then novel compositions and synthesis approaches are merited. However, if the interfaces suppress the long range (DC) conductivity, growing the same material in larger crystals is a promising approach for improving the function of the material.

To design a MOF for light driven applications, it is crucial to understand its photophysics following the absorption of a photon. Optical transient absorption (OTA) and photoluminescence (PL) probe excited states and recombination dynamics, respectively. OTA is a time-resolved technique that measures the changes in a sample's absorption spectrum that occur as a result of photoexcitation. It is sensitive to bound electrons and, as such, can provide information regarding the time it takes for a photoexcited electron to leave the excited system and the time it takes for the system to return to equilibrium. More generally, OTA detects changes in energy states. PL detects photons emitted from optically allowed transitions, including the recombination of charge carriers. PL and OTA can both measure the total lifetime of an excitation, but they cannot determine whether this excitation results in a mobile charge. In contrast to other optical techniques, THz directly measures a

material's photoconductivity. For all-encompassing photoconductivity data, OTA and PL can be used in conjunction with optical-pump THz-probe (OPTP) spectroscopy. OPTP can be performed on the same timescales as these techniques and provides insight into the onset and decay times of photoconductivity.[15] In some materials, electrons undergo internal conversion or hopping steps between leaving the excited system (at a time determined by OTA) and reaching the conduction band (at which point photoconductivity can be detected by OPTP). Furthermore, photoconductivity typically decays much faster than the system returns to equilibrium, meaning there will be a time difference between the decay of photoconductivity detected by OPTP and the recombination detected by OTA or PL. As such, comparisons between OTA, PL, and OPTP timescales can provide information regarding the intermediate steps an electron undergoes before reaching the conduction band and its demobilization mechanisms, thus allowing for the targeted design of MOFs for next generation solar applications.[2]

III. MOFs IN SOLAR APPLICATIONS

One of the most pressing challenges of our time is to harvest and store solar energy sustainably at a low cost.[24,25] MOFs possess outstanding potential to achieve this goal. Most MOFs are synthesized from earth-abundant materials and can be manufactured at low cost.[6] Most importantly, reticular chemistry allows for a vast range of flexible designs.[3,4,26] MOFs can be tailored for specific applications by combining photo-active linkers with redox-active metal centers. However, the final MOF's properties are not a simple linear combination of the ingredients, and to really understand the resulting MOF, we need to understand the physics arising from the interplay of its constituents. THz spectroscopy is an outstanding technique to explore this collective interaction as well as the fundamental physics that determines the macroscopic properties.

Effectively harvesting the sun's energy demands an interplay of several photo-triggered mechanisms and processes.[27] First, the solar light is absorbed and generates an excited electronic state. The excitation energy then needs to be transferred into usable electrical or chemical energy before the excited state recombines. This transport can be detected by its OTA signal or, even better, the resulting photoconductivity. The latter can be measured with OPTP.

A. Requirements for solar energy conversion

A strong overlap between a material's absorption spectrum and the solar spectrum is essential for the efficient conversion of solar energy. Generally, this means engineering the bandgap so that it matches the energy of the photons in sunlight. Band gaps can be tailored through the selection of ligands, nodes, and guest molecules.[28] One commonly used method is the incorporation of chromophores as ligands in MOFs.[2] MOFs can also be tuned for visible light absorption through the incorporation of primary amines. For example, the addition of amino groups to the ligands of MIL-125(Ti) and UiO-66(Zr) resulted in a raising of the valence band energy and pushed the materials' originally deep-UV absorption into the visible range.[7]

Visible light absorption is only one requirement a material must meet to be viable in solar applications. The material must also produce photogenerated charges with desirable redox potentials, and these charges must be located on atoms or molecules that

allow charge transfer. The redox potentials can be measured electrochemically.[7] UV-visible spectroelectrochemistry (SEC) is an established technique capable of monitoring electrogenerated species in solution. Since its first demonstration more than 40 years ago, the technique has been greatly improved and modified for various applications.[29] Moving from the established visible detection to THz detection (THz-SEC) is a relatively new development, with the first THz transparent electrochemical cell being published in 2015.[30] Because THz radiation is mainly sensitive to mobile charges, THz-SEC provides unique insight into the potentiostatic filling of conduction band states.[31] Potential-controlled OPTP measurements are also possible and have been demonstrated as a valuable method for monitoring electron injection efficiency and trapping under an applied voltage and broadband illumination.[30] These measurements provide insight into the filling of trap states and the resulting effect on electron injection into the conduction band.

Crystallinity is crucial for long range transport, as interfaces and boundaries hinder the movement of charge carriers. For photovoltaic applications, the thickness of microcrystalline and thin film devices needs to be matched to the cell requirements. In particular, the MOF must be large enough to absorb a sufficient amount of light but thin enough that the photogenerated charge can be transferred to the electrode or reaction center.[32] The optimal thickness is, therefore, defined by the mobility and lifetime of the generated carrier. Carrier lifetime can be measured via OPTP and mobility via time-resolved THz spectroscopy (TRTS). The combination of both measurements is then leveraged to calculate the optimal size of a photoconductive MOF crystal.[33] This calculation could be confirmed via carrier extraction with acceptor molecules.[32]

B. THz studies on conductive MOFs

Terahertz spectroscopic techniques have proven especially useful for characterizing emerging solar materials such as metal halide perovskites,[34] metal oxides,[35] and 2D materials.[36] There are a few researchers who have used terahertz spectroscopic techniques to directly measure the conductivity and photoconductivity of MOFs for photovoltaic applications.[23,37–40]

In a study by Pattengale *et al.*, the ground state conductivity in Mn_2DSBDC (DSBDC = 2,5-dimercaptoterephthalate) was measured.[23] The MOF's structure is illustrated in Fig. 4. The top portion of this figure shows the infinite Mn–S–Mn–S chains, which provide a through-bond conductivity pathway.[23] A powder sample of Mn_2DSBDC was previously measured using two probe DC measurements.[41] The measured DC value was about 2.5×10^{-10} S/m, while the THz conductivity measured in the newer study was 25 S/m at 1 THz. This huge difference illustrates the clear advantage of THz spectroscopy over DC measurements for novel materials. DC measurements determine the long-range sample conductivity, meaning the electrical contacts between the powder sample and metal pads, as well as the contacts between the individual powder grains, limit the DC conductivity. As a result, the air-powder mixing ratio determines the conductivity of the sample, which makes it impossible to determine the actual conductivity of the material.

THz-TDS as a contact free technique reveals the charge movement within the grains on a sub-micrometer length scale, eliminating the contact resistance and separating the bulk resistance from the grain-to-grain resistance.[13] This provides a much more
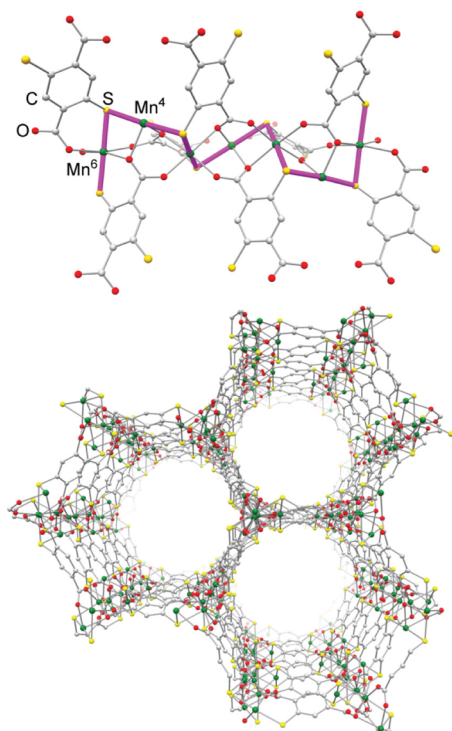
FIG. 4. The x-ray crystal structure of Mn$_2$DSBDC. The top portion illustrates the continuous Mn–S–Mn–S chains, which provide through-bond conductivity. The bottom portion illustrates the infinite 1D pores along the c-axis. Reprinted with permission from Sun *et al.*, J. Am. Chem. Soc. **135**, 8185–8188 (2013).[42] Copyright 2013 American Chemical Society.

accurate estimation of the achievable conductivity in a powder sample, particularly in MOFs. This insight can then be leveraged to design and optimize MOFs without needing to worry about grain sizes and contact effects that dominate DC measurements. This field remains novel, with so far only a single experiment published. Therefore, the core question remains as to how accurate DC value predictions based on THz measurements are.[33] Further studies are needed and remain rewarding due to the novelty of the field.

OPTP is used to measure femtosecond-resolved photoconductivity dynamics. The dynamics reveal the carrier lifetime and can exhibit multi-exponential behavior, which indicates the presence of various trapping and recombination mechanisms that occur on different timescales.[15] Carriers do not necessarily have the same mobility throughout the full duration of photoconductivity; they can exhibit different mobilities in the different decay ranges. The mobility and scattering times of photocarriers can be measured with TRTS. TRTS scans are taken at a set pump delay, meaning a particular time after photoexcitation. Comparing the spectral insight gained shortly after excitation with that gained at later times can shed light on the underlying physics of photoconductivity.[15]

Early work regarding photoconductivity in MOFs utilized microwave measurements. Microwave measurements require larger grain sizes as microwaves reverse polarity once every nanosecond,

while THz changes direction on a sub-picosecond timescale.[33] As a result, the unidirectional charge displacement is on the micrometer scale for microwave measurements and on the nanometer scale for THz. Microwave measurements use electrical systems for the generation and detection of microwave radiation, meaning the on/off time of the electronics limits the time resolution of the measurements (typically to µs and longer). For example, Narayan *et al.* measured the photoconductivity of Zn$_2$TTFTB (TTFTB = tetrathiafulvalene tetrabenzoate), reporting microsecond dynamics.[37] Utilizing OPTP, Pattengale *et al.* demonstrated that ultrafast photoconductivity actually takes place on a ps time scale, as shown in Fig. 5(a).[43] This study also revealed that the previously reported long-living conductivity only accounts for about 3% of the total conductivity, meaning microwave experiments missed 97% of the photoexcitation and crucially underestimated the full potential of the material. In the same study, TRTS was used to measure the spectrally resolved THz photoconductivity of Zn$_2$TTFTB, as shown in Fig. 5(b). The resulting Drude–Smith fit implies that the MOF's photoconductivity stems from a band-like transport mechanism.

One core approach to optimize MOFs for solar applications is to utilize different metal centers to tune their absorption bands.[44,45] Naively, a better overlap with the solar spectrum should lead to better photovoltaic performance. However, THz measurements demonstrate that this tuning also alters the photoconductivity of the MOF.[40] OPTP traces taken for Ni-THQ, Zn-THQ, Cu-THQ, and Fe-THQ (THQ = tetra-hydroxybenzoquinone) indicated that Fe-THQ is 30–40 times more photoconductive than Cu-THQ, while Zn-THQ and Ni-THQ did not exhibit an appreciable THz photoconductivity response. This result indicates that the optical and electrical properties of the MOFs are interconnected. Another interesting finding in this study was that exposure to air over several weeks changed the Fe redox state (confirmed with EPR), which reduced the OPTP signal by more than an order of magnitude. This is particularly exciting as XRD measurements did not reveal a structural change, illustrating that THz can provide significant insight into how redox chemistry alters photoconductivity.[40]

The charge carrier mechanism in a MOF can also be explored directly through TRTS.[46] One study analyzed the complex photoconductivity of a 2D Fe$_3$(THT)$_2$(NH$_4$)$_3$ film (THT = 2,3,6,7,10,11-triphenylenehexathiol).[38] This study found that the complex photoconductivity of the material follows a Drude-type model, meaning it exhibits a band-like transport mechanism. The mobility of this MOF was determined from the best fit Drude model to be 220 cm^2 V^{-1} s^{-1}. This mobility was verified using Hall effect measurements, confirming that a band-like carrier transport mechanism is at play[38] and further demonstrating the complementary relationship between THz and DC conductivity measurements.

Temperature-dependent conductivity measurements can be used to ascertain the factors limiting carrier mobility in a material. Through the comparison of the DC/Hall effect and THz conductivity, it was determined that (1) impurity scattering is the primary limiting factor on the carrier mobility of Fe$_3$(THT)$_2$(NH$_4$)$_3$ and (2) the MOF has a thermally induced carrier population. THz photoconductivity measurements did not exhibit a temperature-dependence, indicating that impurity scattering is the primary factor limiting the MOF's carrier mobility, as phonon scattering is temperature-dependent. Four-probe electrical DC conductivity measurements, however, showed a strong temperature dependence in disagreement
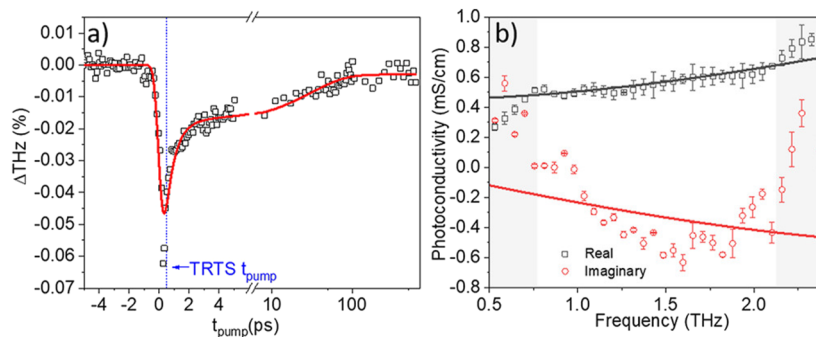
FIG. 5. (a) Typical OPTP trace indicating a representative pump delay selection for TRTS. (b) Photoconductivity measurements with Drude–Smith fit results, taken at a pump delay of 500 fs. Reprinted with permission from Pattengale *et al.*, J. Am. Chem. Soc. **141**, 9793–9797 (2019).[43] Copyright 2019 American Chemical Society.

with the TRTS results. This contradiction indicates the existence of a thermally induced carrier population or temperature-dependent DC mobility, perhaps due to grain boundary effects such as thermally activated inter-grain hopping. Hall effect measurements revealed that the DC mobility is, in fact, temperature-independent, suggesting that thermally activated carriers are the true cause of the four-probe conductivity measurements' temperature dependence.[38] Without the comparison to THz conductivity, it would not be possible to make these determinations.

The carrier lifetime in most MOFs is rather low (on the order of ps), making efficient charge extraction on a solar-cell scale challenging. This challenge can be avoided by using MOFs as a sensitizer on large bandgap semiconductors (e.g., TiO_2). In this geometry, the photogenerated charge travels only a short distance (sub micrometer) before being injected into the semiconductor, resulting in efficient charge separation and usable photo-energy. Zn_2TTFTB has been explored for this purpose through OPTP measurements. The comparison of OPTP traces for the MOF on TiO_2 and the ligand (TTFTB) on TiO_2 indicates ultrafast electron injection from the MOF into TiO_2. This demonstrates that using the MOF as a sensitizer improves its potential for photovoltaic applications. This study demonstrates the utility of THz spectroscopic techniques for monitoring charge extraction from photosensitizers.[39]

C. THz studies on excitons and band structure

Photon energy absorbed by a gas phase molecule creates an excited state still bound to this molecule. In solid states, a similar transition drives charge transfer into an electronic band state. MOFs can exhibit both types of transitions—either bound excitations or mobile charges. The latter case leads to photoconductivity. Unfortunately, bound transitions are often incorrectly referred to as excitons. We would like to emphasize here that an exciton in the solid-state sense refers to a mobile electron–hole pair that has a net charge of zero, while many authors loosely use this term for any photoexcited charge, even when still bound to the original molecule and its orbitals. Excitons commonly exhibit excitonic level transitions in the meV energy (THz frequency) range.

MOFs are often associated with localized bonding and band structures. Their valence and conduction bands can be ligand-

centered or node-centered. In MOF-5, the valence band is node-centered, while the conduction band is ligand-centered.[47] MIL-125 is the opposite, with a ligand-centered valence band and a node-centered conduction band.[47] Other MOFs, such as the zeolitic imidazolate framework (ZIF)-8, have ligand-centered excitations, with both bands being located on the ligand.[47] This highly localized nature makes it difficult to elucidate their band structures and distinguish between bound and free electrons.[48]

Distinguishing between bound and conduction band electrons is often attempted using density functional theory (DFT) calculations.[11] In materials with localized bonding, there are significant difficulties associated with the determination of the optical bandgap. The optical bandgap is the energy of an absorbed photon required for an electron to reach the optically excited state with the lowest energy (LUMO). This state might be localized on a molecule and does not necessarily result in a mobile charge. For photoconductivity, the electronic bandgap—the difference in energy between the valence and conduction bands—is needed.[48] In the case of MOF-5, the electronic bandgap was severely underestimated by initial studies, which approximated it to the optical bandgap. A 2021 study of MOF-5 using the GW approximation and Bethe–Salpeter equation revealed that the optical bandgap of 4.5 eV is, in actuality, only about half the true electronic bandgap of 8 eV.[49] It is often incorrectly stated that this energy difference between optical and electronic bandgaps is the exciton binding energy; however, exciton binding energies are typically on the order of meV, while the difference between optical and electronic bandgaps may be on the order of eV.

The best way to measure an electronic bandgap is to verify that the laser excitation results in photoconductivity. Using a tunable ultrafast light excitation provided by an optical parametric amplifier (OPA), different energies within the optical bandgap region can be selected. For each pump wavelength, the resulting photoconductivity is then measured. In the case of a purely optical bandgap transition, the resulting bound charge will not alter the conductivity. However, if the energy drives an electron from the valence to the conduction band (electronic bandgap), OPTP will detect a clear change in conductivity. This sensitivity to the excitation of electrons into the conduction band is one of the core strengths of OPTP. Similar techniques have been employed in CW–DC photoconductivity
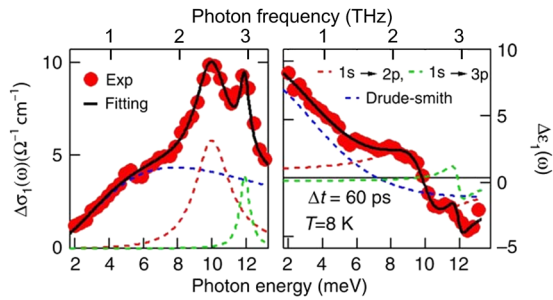
FIG. 6. The THz response function under 790 nm excitation and 60 ps pump–probe delay. The left side shows the conductivity and the right side shows the permittivity. The contributions from the two absorptive resonances can be seen as the red and green dotted lines, where red represents the 1s → 2p transition while green represents the 1s → 3p transition. The blue dotted line is the contribution of unbound (mobile) charges, fitted with the Drude–Smith model. Adapted from Luo et al., Nat. Commun. **8**, 15565 (2017).[53] Copyright 2017 Author(s), licensed under a Creative Commons Attribution 4.0 License.

measurements, where the photoconductivity for different parts of the solar spectrum is measured.[50,51] However, no such work has been done on MOFs.

The utilization of THz spectroscopy to analyze exciton dynamics has not yet been demonstrated in MOFs. There are several reasons for this, namely that defects in the crystal would easily scatter an exciton, dissociating the exciton into an electron and a hole. Secondly, thermal effects could provide excitons with sufficient energy to dissociate. All excitons are unstable with respect to the recombination process, resulting in brief exciton lifetimes.[52]

While it has yet to be demonstrated in MOFs, the Wang group has used THz spectroscopic techniques to analyze intra-excitonic level transitions in methylammonium lead–iodide perovskites (MAPbI$_3$).[53] In MAPbI$_3$, the exciton binding energy ranges from 2 to 60 meV. This had previously been measured using optical techniques sensitive to inter-band transitions, which only measure bright excitons with approximately zero center of mass momentum.[54] With TRTS, however, one can directly probe intra-excitonic level transitions across all momentum-space.[55]

By analyzing the photoinduced THz response function, measured at 8 K, the Wang group found two absorptive resonances as shown in Fig. 6. Excitonic transitions are quantized states described by $E_n = -E_{1s}/n^2$, with n being the quantum number or level of the transition and E_{1s} the zero-point energy. The same quantization was observed experimentally, identifying the measured transitions as excitonic. The exciton binding energy E_{1s} was calculated to be 13.5 meV.[53] This study on perovskites indicates that THz spectroscopy can provide insight on MOFs' exciton binding energies and their band structures. However, such a study would need to be performed at cryogenic temperatures and on defect-free MOF single crystals.

D. Phonon electron interactions

Perovskites commonly exhibit a high defect density, which, for classical semiconductors, would be detrimental to conductivity and carrier lifetime.[56] Despite these defects, perovskites exhibit excellent electrical conductivity and long living photocarriers. Recently,
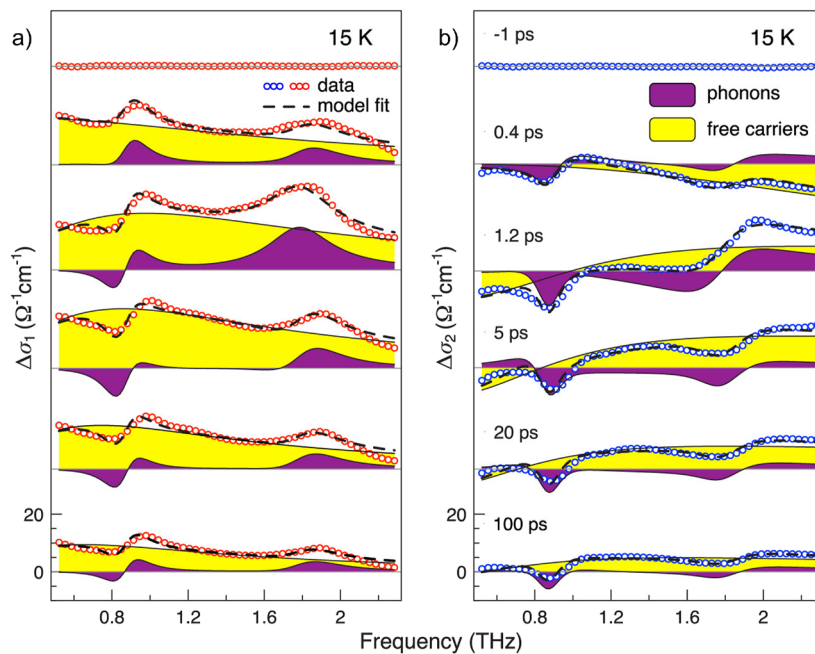

FIG. 7. The (a) real and (b) imaginary parts of the photoconductivity measured at various delay times. Yellow areas represent Drude–Smith contributions, while purple areas represent peak-shift/phonon contributions. Adapted with permission from Zhao et al., ACS Nano **13**, 8826–8835 (2019).[34] Copyright 2019 American Chemical Society.

this paradox was deciphered using TRTS.[34] Zhao *et al.* found that phonon–electron interactions significantly influence the carrier lifetime in these materials. This direct observation of phonon interactions with charge carriers can provide insight into the factors that determine the efficiency of photovoltaic materials.[34]

In this study, a broad-band THz probe pulse was used. This range contains frequencies that are readily absorbed by free carriers in a Drude-type mechanism, as well as the resonant frequencies of low-energy optical phonon modes. This allows TRTS to monitor photoinduced charge carriers and their interactions with phonon modes simultaneously, as shown in Fig. 7. The study found that a large population of phonons at room temperature is responsible for reducing defect trapping of charge carriers. While other techniques can deduce carrier-phonon coupling, TRTS provides information on the dynamics of carriers, phonons, and excitons all in one coherent dataset. TRTS was proven capable of resolving these interactions on a picosecond timescale.[34]

This technique has not yet been employed in the case of MOFs. The exploration of phonon modes in MOFs via TRTS could pave the way for the tuning of their phonon properties such that defect trapping is averted, as is the case in perovskites. This may lead to a substantial improvement in MOFs' photovoltaic capabilities.

IV. GAS-MOF INTERACTIONS AND THz DYNAMIC STRUCTURE

The separation of gaseous mixtures is essential for industry applications and accounts for 15% of global energy consumption.[57] Obviously, a filter needs to be permeable for carrier gases, while absorbing the target gases. The gases in these mixtures typically have similar sizes and physical properties, which makes their separation difficult.[58] MOFs provide an excellent scaffold for the transport of background gas through their structures, while their tunable electrochemistry and pore sizes allow for selective and specific capture of gas molecules. Hence, MOFs for gas storage and separation applications have received substantial attention in materials science.[59–67] Potential applications include CO_2 capture[68] and O_2 purification.[69] Furthermore, MOFs have garnered interest as a means of capturing harmful chemicals and compounds, such as benzene, H_2S, SO_2, and NO_x.[70–72]

Most techniques used to characterize MOFs' efficiency for these applications focus on quantifying their gas selectivity/sensitivity.[73] This approach provides solely a final number and, therefore, limited insight into the physics at play during gas capture. Recent studies on MOFs have focused on the relationship between THz lattice vibrations and the mechanical properties of the material.[74] These studies have utilized inelastic neutron scattering and synchrotron far-infrared measurements, which have a low signal-to-noise ratio at THz frequencies compared to THz-TDS.[75] As such, THz-TDS has the capability to provide low frequency information that has previously been overlooked.

A. THz studies on MOFs for gas storage/separation

Molecular visualization is often based on static chemdraw images and XRD data. This rigid picture wrongly suggests that molecules are fixed in place. In reality, everything is moving at room temperature, which is especially true for organic molecules.

MOFs are constantly breathing and opening/closing the gates to the framework. This dynamic landscape is crucial for gas adsorption and the penetration of molecules into the framework. The collective motions are associated with meV energies and, therefore, lie firmly in the THz range.[14,19,76] As such, THz measurements in combination with DFT calculations provide an excellent pathway to understanding the dynamic structure.[20,77] A change in the MOF, in particular the filling of its pores with gas, will alter the vibrational modes. Simply put, a framework will breathe differently when filled.

Low frequency, long range THz modes in MOFs are particularly relevant to the properties and function of the material. In addition to the gate-opening effect discussed above, phase transitions[78] and a MOF's response to temperature and pressure[79] are dependent on these vibrational modes. Terahertz spectroscopy can be used to identify and characterize these low frequency vibrational modes, providing materials scientists with essential knowledge for the modification and utilization of MOFs in industry applications.

Low frequency spectroscopic techniques have been used to study the vibrational modes of various zeolitic imidazolate frameworks (ZIFs).[74,80] THz-TDS is ideally suited to ZIFs, which have collective atomic motions lying in the terahertz range.[75,81] Because these motions are reliant on the material's potential energy landscape both within a single molecule and across many molecules, THz-TDS can provide an abundance of information regarding the interactions within the material.[75]

ZIF-8 is one of the more widely explored MOFs. The effects of temperature and pressure on its adsorption capacity have been studied using a variety of techniques.[82–85] Inelastic neutron scattering (INS) in combination with XRD and DFT calculations has been used to show an adsorption-induced change in the structure of ZIF-8 at low pressures. At these pressures, the ligands of the MOF rotate such that its accessible pore size is increased. The interatomic distance thus increases from 2.9 to 3.4 Å.[86] This is an example of the gate-opening effect, which provides the material with exciting attributes such as molecular selectivity and sensing ability.[87,88] The displacement of the linkers, like any large range displacement of molecular subunits, occurs at terahertz frequencies.[89] It stands to reason that the terahertz vibrations and mechanochemical properties of MOFs are interconnected.[90,91]

Zhang *et al.* utilized THz-TDS to confirm the previously controversial low frequency designation for the gate-opening movement of the ligands in ZIF-8.[74,80] Visualization of the DFT modes shows that the excitation at 2 THz is associated with gate-opening. Experimental results from THz spectroscopy confirm the predicted spectra. As shown in Fig. 8, the characteristic mode at 2 THz is suppressed when the MOF is loaded with nitrogen. Nitrogen is an inert gas, meaning it does not chemically alter the MOF. The suppression thus serves as additional confirmation that this mode is mechanically hindered by nitrogen in the MOF's pore. The result demonstrates the value of THz spectroscopic techniques for monitoring structural changes in a non-invasive manner.[75]

In the context of gas separation and storage applications, THz has been used to probe the effects of gas adsorption. In one study, the terahertz transmission spectra were used to analyze the adsorption behavior of hydrocarbon gases in ZIF-8.[81] The MOF's transmission spectrum was taken after exposure to ethane, butane, and carbon
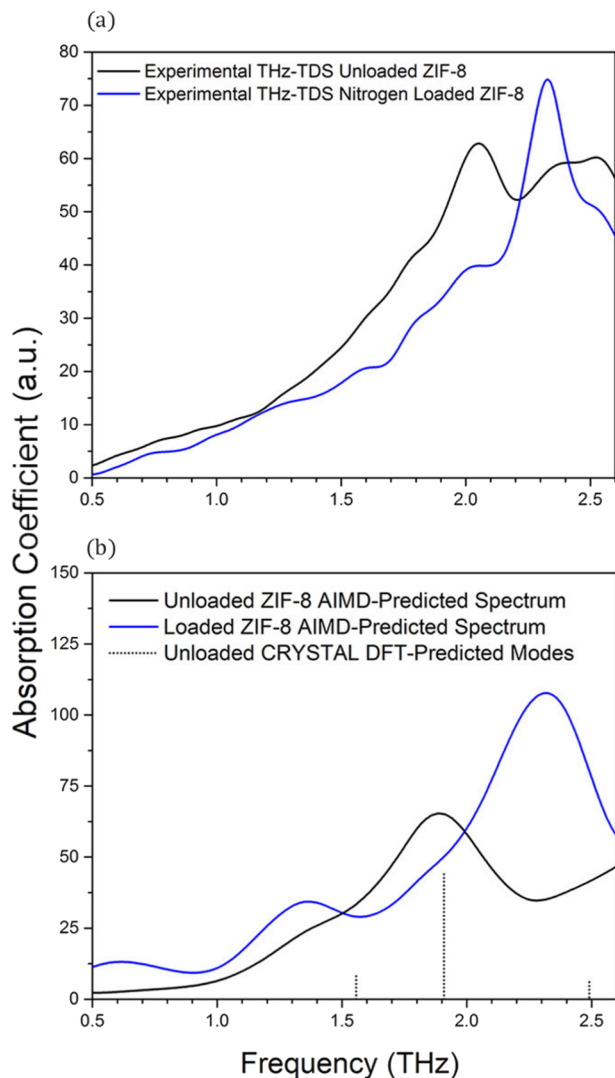
FIG. 8. (a) Experimental and (b) AIMD predicted THz absorption spectra at 97 K. Black represents unloaded ZIF-8, while blue represents ZIF-8 loaded with N_2 at 80 bars. Adapted with permission from Zhang *et al.*, J. Phys. Chem. C **122**, 27442–27450 (2018).[75] Copyright 2018 American Chemical Society.

FIG. 9. THz transmission spectra of ZIF-8. Black represents ZIF-8 purged with nitrogen, while red represents ZIF-8 exposed to ethane. Measured at room temperature under 1 atm pressure. Adapted with permission from Tanno *et al.*, J. Phys. Chem. C **121**, 17921–17924 (2017).[81] Copyright 2017 American Chemical Society.

V. CONCLUSION AND OUTLOOK

Photoconductive metal organic frameworks combine low weight, low cost, ease of fabrication, and tunability into an exciting and promising new class of materials for solar applications. To guide the research toward even better materials, we highlighted the core insights that THz measurements can provide. THz spectroscopy measures ultrafast conductivity, which can be orders of magnitude higher than microwave or DC measurements that are limited in their temporal resolution and measure multigrain properties. THz spectroscopy provides a more microscopic picture of conductivity in a novel material, separates intra- and inter-grain effects and, therefore, uncovers the material's true potential. This can be clearly seen by the studies on Mn_2DSBDC and Zn_2TTFTB, in which the THz conductance/photoconductance values were 11 and 2 orders of magnitude higher than previously reported values, respectively.

A second field of promising applications for MOFs is gas separation and storage. THz spectroscopy in combination with DFT provides a detailed picture of guest-MOF interaction. The adsorption of gas molecules alters the low energy vibrations. This is clearly demonstrated by the various changes in THz modes when the MOF is exposed to different gases. This field is still in its infancy, and future work will provide outstanding insight into the physics at play. The current approach of designing pore sizes to fit the gas size will be augmented by the detailed understanding of the dynamic structure and binding energies provided by THz spectroscopy. This will lead to significant improvements in the gas separation and storage capabilities of MOFs.

Overall, terahertz spectroscopy is a unique tool for determining various properties of a material with little sample preprocessing required. It can probe the small-scale, inherent properties of MOFs with sub-picosecond time resolution. The technique has proven its utility in materials science, and its expansion into the world of MOFs is only just beginning.

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dioxide. In the cases of ethane and butane, the 2 THz vibrational mode was suppressed, as shown in Fig. 9. It was thus inferred that the ligands' motion is influenced by gas adsorption, resulting in a decreased intensity of the 2 THz peaks associated with the gate-opening effect as discussed previously. When the MOF was exposed to nitrogen gas after ethane, the transmission spectrum remained shifted, indicative of a more rigid binding than just adsorption, causing an irreversible structural change in ZIF-8.[81] This study demonstrates the capabilities of THz-TDS in monitoring adsorption-induced changes in MOFs, a crucial first step toward in-operando monitoring of gas filters.
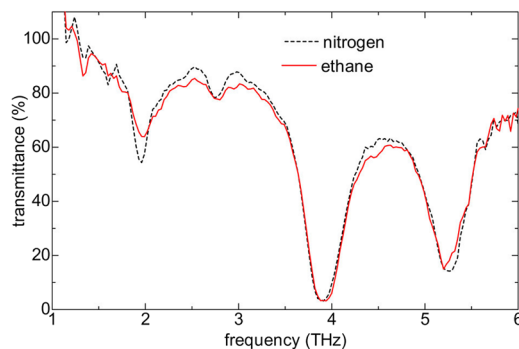
AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Kendra Hamilton: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Resources (lead); Software (lead); Validation (lead); Visualization (lead); Writing – original draft (lead); Writing – review & editing (supporting). **Jens Neu**: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Funding acquisition (lead); Investigation (lead); Methodology (lead); Project administration (lead); Resources (lead); Software (lead); Supervision (lead); Validation (lead); Visualization (lead); Writing – original draft (supporting); Writing – review & editing (lead).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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