January 2022

The Development Of Fundamental Insights Into The Electronic Behaviors Of Next-Generation Materials

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THE DEVELOPMENT OF FUNDAMENTAL INSIGHTS INTO THE ELECTRONIC BEHAVIORS OF NEXT-GENERATION MATERIALS

by

SYDNEY NICOLE LAVAN

DISSERTATION

Submitted to the Graduate School of Wayne State University,

Detroit, Michigan

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

2022

MAJOR: CHEMISTRY (Physical)

Approved By:

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Advisor Date

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DEDICATION

To my younger self, my current self, and my future self; this journey has taught me that I am worthy. And, to my family, friends, advisors, and coaches for shaping me into the young woman I am today.
ACKNOWLEDGEMENTS

The young woman and scientist I am today is unrecognizable compared to who I was when I started my PhD journey 4.5 years ago. The subject of chemistry, specifically physical chemistry, sparked a huge interest of mine during my undergraduate studies. I loved the connection between something I cannot see (quantum mechanics) to the physical world and the theory behind it in addition to how diverse the subject is and how involved it is in our everyday lives. I knew the chemistry field was something I was passionate about and what I wanted to pursue for the rest of my life. I came to Wayne State University not knowing I would gain advisors who are tremendous scientists as well as people, colleagues who are just as passionate about the chemistry world and who have become lifelong friends, a community where we are all committed to excellence in science and supporting one another, and finally I’ve come to love the state of Michigan and calling it home. To survive and complete a PhD in chemistry is no easy task, and it takes a village to succeed.

I would first like to thank and acknowledge the entire Department of Chemistry here at Wayne State University. From the front office staff, Melissa Rochon our academic coordinator, Jackie Kennedy our facilities coordinator, the business office, the science store office, and all the advisors and research staff. Everyone in this entire department plays a huge role in the success we graduate students attain. I would like to thank Aaron S. Rury and Zhenfei Liu my coadvisors. Under the guidance of both Aaron and Zhenfei, I grew tremendously not just as a scientist but also as a young woman. I would like to thank them for pushing me at the times I needed it and for always seeing the potential in me. They have helped me develop valuable skills I will take with me for the rest of my life and career. I would like to thank my other committee members, H. Bernhard Schlegel,
Young Hoon Ahn, and Alex Matos Abiague for their time and effort in helping me prepare for my final defense. I would like to thank the members of both the Rury and Liu group as well as my other colleagues throughout the department. We have all bonded through this PhD journey and supported each other every step of the way. I am now walking away with lifelong friendships that I am forever grateful for.

Completing a PhD does not just involve the department, your advisors, and colleagues. Without the support from my family and friends, I can confidently say I would not be the scientist and young woman I am today. I would first like to thank my mom Tanya Lavan, my dad Fran Lavan, my sister Olyvia Lavan, and my brother Griffen Lavan. I would like to thank my grandmother Deborah Pierce and my aunt Donna Braithwaite and uncle Mike King. The family members I’ve named and those I did not (as my family is huge!) all have played a significant role in my life and supporting me during my PhD. I would also like to thank my friends who have stuck by my side and supported me this entire time. My closest and lifelong friends from Monmouth University, Kristen, Danielle, Monique, Julie, Allie and Miranda, my crossfit crew and soccer/volleyball friends I have gained here in MI, and my MotorCity church friends who I now consider my second family. I thank each and every one of them and I am truly blessed to have such tremendous friends in my life.

Finally, before my passion of science and chemistry developed my first passion was and still is soccer. First, I would like to thank my parents for all the traveling we did to support my dream and passion I had for soccer. Introducing sports into my life at a young age has allowed me to become the successful young woman I am today and I am forever grateful I had the opportunity to be heavily involved with sports growing up. I ultimately was offered a scholarship to play D1 soccer for Monmouth University where I competed to play at the highest level attainable in the NCAAs. I would like to thank all my coaches I’ve had along the way especially Dr. Krissy Turner
the head coach at Monmouth University and Kylee Flynn the associate head coach at Monmouth University. The environment they created at Monmouth where I was pushed towards excellence and the mentality instilled in us as players has helped my transition into a PhD chemistry program with the mindset I needed in order to be successful.
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Figure 50

Figure 51

Figure 52
CHAPTER 1 INTRODUCTION OF NEXT-GENERATION MATERIALS

In this work we provide fundamental insights into the electronic behaviors of next generation materials. The development of such insights will allow one to begin to understand the mechanisms that drive their future applications in energy storage and energy efficiency. Energy storage and energy efficiency is important as the world population continues to grow and expand. This has led to the exploration of different sources of energy found in our environment which include solar and wind power. The demand to meet our expanding energy needs requires the development of new next-generation materials. The challenges that arise in providing sufficient energy, however, are among the most difficult to overcome. We have yet to discover the ideal material, nor have we achieved a sufficient understanding of the energy-conversion mechanisms.

The three main forms of energy systems we have include: batteries, capacitors, and fuel cells. The Ragone plot is an excellent interpretation of different energy storage systems we have [1, 2, 3]. The Ragone plot is used to compare the performance of various energy storage devices. Figure 1 is an example of a typical Ragone plot. We have the power density on the y-axis, the energy density on the x-axis and the labeled energy systems. Each energy system has their unique characteristics and structure-property relationships related to their energy applications. When we compare capacitors and batteries, we find batteries have a higher energy density than capacitors, but a capacitor has a higher power density than a battery [4]. This difference stems from batteries’ capability to store more energy, however, a capacitor can give off energy more quickly. Batteries are thought of as the slow movement of charge carriers and are classified in the long term category, while capacitors are categorized as short-term energy storage devices [5, 6]. Ideally, we need to begin to bridge the gap between having high power density and high energy density technology to
meet the energy demands we face in achieving a desired functionality.

Figure 1: Prototypical Ragone plot comparing the performance of a battery, a capacitor and a fuel cell.

The first step in bridging this gap is understanding how the material influences its structure and thus its properties and performance; hence, the structure-property relationships. This research begins to bridge the gap between experiment and theory to provide insights into the electronic behaviors that will establish the structure-property relationships. To improve devices that store and consume energy, we researched three materials: antiferroelectric materials; 2D hybrid organic-inorganic perovskites (HOIPs); and metal organic frameworks (MOFs). These materials all have distinct structures that make them ideal for the focus of our studies.

Hydrogen-bonded antiferroelectric crystals possess relatively large dielectric constants, and can serve as solution processed materials for energy storage technologies [7]. Antiferroelectric materials are a subset of dielectric materials. Dielectric materials can be utilized between the plates of a capacitor to provide separation which increases the capacitance or the ability to store
energy [8, 9]. In dielectric materials, the atoms or molecules experience both the external applied field and the field produced by the dipoles [10]. Therefore, the arrangement of the dipoles plays an important role in the materials ability to store energy. The spontaneous antiparallel arrangement of the dipoles in antiferroelectric materials have the capability to increase the amount of charge stored in a capacitor and this makes them ideal for studying.

Figure 2 shows the hysteresis loop for an antiferroelectric material taken from reference 11 [11]. This hysteresis effect plays a role in the energy storage capability where this plot shows the polarization vs the electric field dependence. The particular features observed in the hysteresis loop for antiferroelectric materials, such as the double loop and shape of the loop, contribute to its energy storage capability [12]. The energy efficiency of these materials are thought of as the ratio of the recoverable energy density to the total stored energy density [12, 13, 14]. Antiferroelectrics have a larger recoverable energy density compared to ferroelectric materials [12, 14]. Despite these results seen throughout the research community, material chemists lack direct connections between the structure-property relationships with regards to the electrostatics of these antiferroelectric materials. We focus our attention on relating the microscopic electrostatics of the antiferroelectric material of interest to its macroscopic properties.

The appeal of 2D HOIPs is related to its structure and environmental stability compared to the traditional 3D structure [15, 16]. The tunability of the 2D HOIPs makes them a desirable candidate in applications for light emitting diodes and photovoltaics [17, 18]. These 2D lead halide HOIPs possess broadband and narrowband features in their photoluminescence (PL) experimental measurements. Figure 3 shows the experimental work done by Booker and coworkers. This group investigates the origin of this attractive broadband feature they observe [19]. The broadband feature could potentially be utilized for white light emission [20]. However, the detailed mechanism
driving these features observed in the PL spectra remains unclear. In addition, white light emitting 2D hybrid perovskites contain a wide array of different organic spacer molecules. This has also limited the efforts into understanding the mechanism with regard to compositional and structural effects.

Throughout the 2D hybrid perovskite community there are two widely accepted and studied mechanisms that contribute to the PL features. The two mechanisms stem from self-trapped excitons and defects. It is known that when these 2D hybrid perovskites are excited with light, the octahedral framework can become distorted. This distortion plays a role in the mechanism involved with the self-trapped excitons. Figure 4 is a simple illustration of the corner sharing octahedral distortion before and after excitation. There have been efforts made in understanding the electrostatics of this distortion as well as how this octahedral framework can be engineered [21, 22].

Figure 2: Hysteresis loop for an antiferroelectric material. This figure was taken from reference [11].
Figure 3: (a) Hexyl-ammonium lead iodide temperature dependent transient photoluminescence measurement. (b) Dodecylammonium lead iodide temperature dependent transient photoluminescence measurement. This figure was taken from reference [19].

Figure 5 shows a simple diagram explaining the two mechanisms, self-trapped excitons and defects. Excitons are the charge carriers present in these perovskites. An exciton is the bound state of an electron and hole pair attracted by the Coulombic interaction [23]. Self-trapping occurs when electrons and holes are photo-generated and from there will quickly become self-trapped [24]. This self-trapped state is more stable. The yellow ball in Figure 5 represents a charge carrier. For figure 5 (a) we have the pristine structure in red on the left then we can see a distortion in the plane on the right where the carrier is now trapped. This is intrinsic self-trapping of the charge carrier. Figure 5 (b) represents a defect. We can see on the left plane in blue there is a defect present in the material. Then after excitation the charge carrier becomes trapped in the defect site. Figure 5 (c) is similar to that of the (a) except is it extrinsic. This can be thought of as the self-trapping nature influenced by the local nonuniform areas [20]. A practical example of this is if we have a 2D hybrid perovskite with two different halides where one halide can act as a defect, an extrinsic self-trap. Differentiating between an intrinsic and extrinsic self-trapping mechanisms have proven to be difficult using optical spectra [20, 25]. We focus our attention to first understanding the electrostatics between the organic spacer molecules and the octahedral
Figure 4: The blue diamonds represent the simple octahedral framework with the purple circles representing the metal atom such as lead, and the green circles representing the halide atom such as iodine. We have the pristine framework before excitation and the distorted framework after excitation.

framework and then proceeding with the roles defects play in the light emission of our material.

MOFs are unique tunable porous like materials where one can combine different linker molecules and different metal centers [26, 27]. MOFs are therefore excellent candidates in a variety of applications which includes, catalysis, adsorption and separation [28, 29, 30]. Specifically, the adsorption and separation of light hydrocarbons make these materials ideal in fuel energy storage applications.

Sholl and colleagues explored the effect of varying the metal atom present in the MOF M-1,3,5-benzenetricarboxylic acid (M-BTC) and the molecular binding energies of five small molecules. Figure 6 shows the results from their study. The five small molecules of interest are H₂O, CO,
Figure 5: (a) The intrinsic self-trapping mechanism. (b) The trapping at a defect site. (c) The extrinsic self-trapping mechanism. The figure was adapted from reference [20].

C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$. Their results indicate the binding energies vary widely among the different metal centers chosen. C$_2$H$_6$ has the lowest binding affinity for each case which they attribute to the strong influence by the dispersion interactions associated with the linkers. When they compare the different metal centers, Cr, Mo and Cu have the lowest binding energies [31]. The results of this study begins to tackle the impact of metal substitution in one specific MOF and shows the tunability of the material. One interesting artifact of this study and other MOF studies are pores that have open metal sites. It is seen in the research community MOFs with open metal sites poisons the framework structure after adsorption [32]. This would therefore not be ideal in gas adsorption and separation applications. We focus our attention to studying MOFs without open metal sites where the framework is retained after adsorption [33].

All three materials are relatable in terms of energy storage. The forms of energy antiferroelec-
Figure 6: The structure of the M-BTC MOF and the metal center binding site. The plot shows the binding energies on the x-axis of the 5 small molecules and 5 different metal centers on the y-axis. This figure was adapted from reference [31].

tric and perovskite materials possess are related to their electrostatics (antiferroelectric - hydrogen bonds; perovskites - charge carriers). Alternatively, the form of energy found in MOFs stems from their chemical bonds instead of electrostatics. Our goal for each of these materials is to understand their microscopic electronic behaviors to gain insight into their mechanisms driving such energy-related applications. In doing so, we leverage vibrational spectroscopy and first-principles calculations to showcase our insights.

The work proceeds as follows: chapter 2 we discuss the antiferroelectric material of interest, the research methods we used, our results, and our significant findings. Chapter 3 is dedicated to first understanding the structure and coupling of the layers of 2D hybrid organic-inorganic perovskites. Then we move into the role defects play in these materials. The research methods, results, and significant findings will be discussed. Chapter 4 focuses on metal organic frameworks. We discuss the structures studied, research methods, results, and lastly our significant findings. The last chapter, chapter 5, is dedicated to the conclusions we have made thus far for each material.
CHAPTER 2  ANTIFERROELECTRIC MATERIALS


2.1  BACKGROUND AND PREVIOUS LITERATURE

There remains great interest in interpreting how materials formed from solvated molecular constituents can be used in energy applications [34] such as light generation [35, 36], photo-voltaic conversion of solar energy [37, 38], and electrostatic energy storage [39, 40, 41, 42, 43, 44, 45, 46, 7]. The materials are easy to fabricate and have a non-toxic composition. In particular, studies indicate hydrogen-bonded antiferroelectric crystals comprised of a single molecular species could serve as solution processed materials for energy storage technologies [7]. In addition to possessing relatively large dielectric constants and necessitating high applied electric fields to saturate their dielectric response, the antiferroelectric order of some self-assembled hydrogen bonded molecular materials could revolutionize energy technologies. Specifically, the highly nonlinear polarization response and small polarization hysteresis of antiferroelectrics suggest these materials possess significantly better energy storage capabilities than their ferroelectric and paraelectric counterparts[47]. Despite this interest in using materials comprised of non-bonded molecular constituents, so-called molecular materials, for energy storage applications, materials chemists and physicists lack the direct connections between the microscopic and macroscopic physical proper-
Figure 7: Microscopic crystal structure of the antiferroelectric phase in the $ac$-plane of 2-trifluoromethylbenzimidazole (TFMBI) showing intermolecular hydrogen bonds as red dashed lines, which most align with the crystal’s $c$-axis. Dynamic disorder caused by the free rotation of the methyl group results in the appearance of 6 F atoms on adjacent TFMBI molecules.

In particular, the stability of the antiferroelectric phase of materials like TFMBI, a known hydrogen-bonded antiferroelectric material whose structure is shown in Figure 7 [41], and related single component molecular crystals depends on specific networks of hydrogen bonds. Despite this well known fact, it remains unclear how any changes to the structure or strengths of solid-state hydrogen bonds in materials like TFMBI manifest themselves in their physical observables. In particular, while one may rationalize the hydrogen bonds of TFMBI strengthen as the material contracts upon cooling, one cannot conclude precisely this change affects the electron density of each TFMBI molecular constituent. This deficiency in a fundamental picture of the role of microscopic hydrogen bonding in macroscopic material properties stems in part from the lack of established probes capable of sensing how these materials behave on microscopic lengths scales.
However, the use of molecules as constituents in electrostatic energy storage materials enables the prospects of using molecular vibrations as microscopic, physical probes. To our knowledge, no studies have assessed such an approach for a molecular antiferroelectric previously. Furthermore, while physical phenomena such as shifting peaks in the Raman and IR absorption spectra has been assigned to changes in electronic bond densities due to changes in hydrogen bonding strengths [48, 49, 50, 51] and the vibrational Stark effect [52, 53, 54], anharmonic interactions between different vibrational modes can also change with an external stimulus and cause a shift of any particular peak in a vibrational spectrum measured experimentally. While these different physical mechanisms all produce peaks that shift in vibrational spectra, their respective theoretical formalisms provide a means to decipher the dominance of a particular effect in a given spectroscopic experiment.

Specifically, to account for a vibrational Stark effect due to the presence of a microscopic electric field correctly, one must treat anharmonic contributions to the molecular interatomic potential energy, $U(Q)$, up to third order in the same vibrational normal coordinate for which one observes the peak shift [55, 56]. These so-called mechanical anharmonic terms appear as $(\partial^3 U/\partial Q_i^3)_{0}$ in the Taylor expansion of the interatomic energy in terms of the molecules normal coordinates and cause first order corrections to the energies of the ground and first excited vibrational states of the mode $Q_i$. For the case of bond polarization models, one must introduce non-zero second order contributions from the expansion of the molecule’s dipole, $\mu$, or polarizability, $\alpha$, to cause the first order energies corrections necessary to account for the shift of the ground and excited vibrational states. Despite this difference, those second order corrections should also correspond to derivatives along a single vibrational normal coordinate $Q_i$, i.e. $(\partial^2 \mu/\partial Q_i^2)_{0}$ or $(\partial^2 \alpha/\partial Q_i^2)_{0}$. In contrast to both of these physical mechanisms, anharmonicity can also couple the vibrational modes along different normal coordinates and shift the peaks in a vibrational spectrum upon changing a sam-
ple’s temperature [57, 58, 59, 60, 61, 62, 63, 64]. In the case of this structural anharmonicity, one needs third and fourth order terms in the expansion of the material’s interatomic potential energy like \( \left( \frac{\partial^3 U}{\partial Q_i \partial Q_j \partial Q_k} \right)_0 \) and \( \left( \frac{\partial^4 U}{\partial Q_i^2 \partial Q_j^2} \right)_0 \) to produce first order corrections to the energy levels of the participating vibrational states. Based on these considerations, we seek to explain the fundamental physical mechanism by which peaks in the vibrational Raman spectrum of crystalline TFMBI shift upon changing the material’s temperature. Through the analysis of our results we seek to assess what role any changes to the hydrogen bonding network in TFMBI caused by thermal contraction can be used to understand the material’s structural dynamics. While the shifts of aromatic ring vibrations of similar molecular systems have been attributed to different physical mechanisms such as hydrogen bond-induced polarizations and the vibrational Stark effect, we seek to establish if these assignments can be extended to TFMBI.

### 2.2 RESEARCH METHODS

**Sample Preparation and Structural Characterization**

TFMBI was purchased from Combi-Blocks and purified using the approach reported by Horiuchi et al [41]. Specifically, a 50/50 mixture of methanol (10mL) and distilled water (10mL) in a beaker was heated to dissolve TFMBI to the point of saturation. This process created a dark yellow solution. We allowed the solution to cool and observed the appearance of white powder/crystals. We ran the purified solution through a Buchner funnel and collected the solid sample with filter paper. This process was repeated four times. After the fourth recrystallization we dissolved the newly collected sample in a small amount of ethanol. The resulting solution was left in a fume hood covered partially to crystallize by solvent evaporation. Following several days crystals like the one shown in the inset of Figure 8 formed.

Powder X-ray diffraction (XRD) was used to identify the phase purity of our TFMBI samples.
To make these measurements, we ground the purified TFMBI crystals into a fine white powder. Powder XRD measurements were collected with a Bruker D2 Phaser diffractometer operating at 30 kV and 10 mA, employing Cu K\textalpha\ radiation (\(\lambda = 1.5418\ \text{Å}\)). Diffractograms for structural analysis were collected in the 8-80° 2\(\theta\) range using a step size of 0.0122° and a step time of 1.125 s. LeBail analysis[65] of powder XRD patterns was conducted using the General Structure Analysis System 1 (GSAS-I)[66]. The following parameters were refined: (1) scale factor; (2) background, which was modeled using a shifted Chebyshev polynomial function; (3) peak shape, which was modeled using a modified Thompson-Cox-Hasting pseudo-Voight function[67]; (4) lattice constants; and (5) an isotropic displacement parameter (U\text{iso}) for each atom. We used difference curves, R\text{wp} and residuals to assess the quality of the refined structural models, as shown in Figure 37 in Appendix A.

We identified a suitable single crystal and collected diffraction data on a Rigaku Synergy diffractometer using Cu K\textalpha\ radiation while maintaining a sample temperature of 100 K. We performed unit cell determination, data integration, scaling and processing with Rigaku CrysAlisPro software. Using the SCALE3 ABSPACK scaling algorithm we corrected for X-ray absorption and scaling with spherical harmonics and solved the material structure with the SHELXT [68] structure solution program using intrinsic phasing. We refined the resulting structure with the SHELXL [69] refinement package running under Olex2 [70] using least squares minimization. We deposited crystal data in the Cambridge Crystallographic Data Centre with number 2001167 and generated images of structures using VESTA.[71]

**Raman Scattering Spectroscopy Measurements** To acquire high resolution Raman spectra of crystalline and solution-phase TFMBI, we used a Horiba XploRA Plus Raman micro-spectrometer
fitted with a 10x microscope objective. TFMBI single crystals were excited at 532 nm and collected light emission was dispersed with 2400 gr/mm diffraction grating to produce spectra with 0.7 cm\(^{-1}\) resolution. We measured Raman spectra at 15 different temperatures between 363 K and 78 K. The sample temperature was controlled with a Linkam THMS600 temperature stage. The sample was held at each new temperature for 5 minutes to stabilize before data collection. Solution phase samples were prepared in a fume hood and then transferred into a 1 mm path length cell for spectroscopic measurements. Each solution phase measurement was made with the incident laser focus at a spot within the first 100 µms of the top interface between the solution and spectroscopic cell. Measurements on each solution were repeated several times to ensure reproducible shifts in the Raman peaks of interest. Properties of the experimentally measured peaks were determined from nonlinear least squares fitting to Lorentzian line shapes.

**Density Functional Theory Calculations of the Vibrational Spectra of TFMBI** We calculated the Raman spectra of crystalline phase TFMBI using DFT with the Perdew-Burke-Ernzerhof functional [72] for both correlation and exchange, but with the maintenance of 1/3 exact Hartee-Fock exchange [73], as implemented in CRYSTAL17 [74]. We found the best agreement between theory and experiment using the carbon 6-21G* [75], hydrogen 3-1p1G [76], nitrogen 6-31d1G [76] and fluorine 7-311G [77] polarizable basis sets. Before we calculated the vibrational frequencies using the Coupled Perturbed/Kohn-Sham algorithm [78, 79], we optimized the geometry of atomic positions while maintaining the unit cell parameters established from previous single crystal and our own powder X-ray diffraction studies [41]. To compare the calculated spectra to our experimental measurements, we scaled the computed frequencies by 0.955, which we believe corresponds to accounting for the shifts due to anharmonic effects.
2.3 RESULTS FROM RAMAN MEASUREMENTS

First we assessed the anisotropic structure of TFMBI, specifically the N-H bonds. The structure of the TFMBI unit cell in Figure 7 shows the N-H bond of each molecular constituent nominally points along the c-axis of the crystal. This highly anisotropic structure suggests polarization dependent vibrational spectroscopy experiments can be used to connect the microscopic structure of the material to the macroscopic scales of the lab frame in which we carry out the measurements. Figure 8 shows our test of this proposition. We find the Raman scattering intensity in the region around 3000 cm$^{-1}$ is nearly 10 times larger when we align the electric fields of the incident and scattered beams along the long axis of TFMBI single crystals, like the one shown in the figure’s inset. This difference indicates the long axis of the macroscopic crystal corresponds to its c-axis in the microscopic unit cell. Furthermore, we can use this assessment to correctly compare the vibrational spectra we excite in different spectral regions to the Raman intensities computed with DFT stemming from modulations of the unit cell’s polarizability by atomic motions along the c-axis of the crystal, which we denote as $\partial \alpha_{cc}/\partial Q$.

In addition to the crystallographic information, the properties of the peaks corresponding to the N-H stretching vibration of TFMBI indicate a significant hydrogen bonding interaction in the crystal. We show these interactions in Figure 7 as dashed red lines by modeling any hydrogen bonds as stemming from N and H atoms separated by at least 1.5 Å. The strength of this hydrogen bonding interaction manifests itself in the Raman spectra of Figure 8 through the nearly 400 cm$^{-1}$ red-shift of the N-H stretching vibrational frequency found in the crystalline phase relative to the TFMBI monomer when dissolved in solution, as shown in Figure 38 shown in appendix A. Specifically, we find a broad peak in the Raman spectrum of TFMBI molecules dissolved in DMF
centered near 3480 cm\(^{-1}\), almost 400 cm\(^{-1}\) to the blue of the peaks. In addition to this significant red shift of the peak positions, Figure 8 shows the larger signal in the VV-polarized spectra allows us to resolve the sidebands often present on the red side of N-H and O-H peaks due to hydrogen bonding \([80, 81, 82]\).

The bottom panel of Figure 8 compares the Raman spectra we measured experimentally and computed with DFT in the region around 3000 cm\(^{-1}\) and further supports our assignment of the vibrational origins of the peaks in its top panel. Specifically, our DFT calculations predict the asymmetric N-H stretch on adjacent TFMBI molecules appears at 2992 cm\(^{-1}\) with no scaling of the computed frequency axis. In addition, the peak in the Raman spectrum corresponding to this vibration possesses the highest intensity in this spectral. In addition to the observed polarization anisotropy of the peak intensity we believe this comparison suggests the peaks near 3100 cm\(^{-1}\) correspond to the N-H stretching vibrations and not to C-H stretches often observed with narrow line widths \([83, 84]\).

The delineation of the crystallographic axes of our sample within the frame of the lab in which we carry out our experiments provides a sound means to assign the spectra computed with DFT methods to those we measure in the more congested ring stretching regions between 900 cm\(^{-1}\) and 1600 cm\(^{-1}\). This assignment then gives us the atomic motions involved in the vibrations associated with the experimental peaks and insights into the anharmonic mechanisms taking place in our samples.

We begin with the examination of the spectral region around the strongest peaks observed in the Raman spectra of TFMBI, which lie near near 1000 cm\(^{-1}\), and assign the atomic motions associated with these peaks found from DFT calculations. Next, we study changes to peaks near 1260 cm\(^{-1}\) and 1400 cm\(^{-1}\), respectively, and determine to which atomic motions we should assign
Figure 8: Top panel: comparison of polarized Raman scattering spectra along two separate directions of a TFMBI single crystal indicating the strong anisotropy of peaks near 3100 cm\(^{-1}\). Top inset: comparison of a micrograph of a typical TFMBI crystal grown with the technique described in Methods section above to electric field polarization directions V and H of the laboratory frame used to measure the spectra in the main panel. Bottom panel: comparison between the cc-polarized Raman spectrum calculated with DFT (red) and the experimentally measured spectrum at 298 K in the VV polarization configuration (blue). Bottom inset: atomic motions comprising a calculated vibration found at 2992 cm\(^{-1}\) from DFT calculations corresponding to the most intense peak in the calculated spectrum of the top panel.
these peak. Lastly, we investigate the thermally dependent properties of peaks near 1550 cm$^{-1}$ and describe the atomic motions we propose cause their presence in the experimental spectra. After presenting the results in each region we then develop a theoretical model to explain the observed trends in peak positions within each region as a function of the sample temperature.

The Raman spectra of crystalline TFMBI of the different regions are shown in figure 9. The top left panel compares the Raman spectra of crystalline TFMBI in the region around 1000 cm$^{-1}$ at five representative sample temperatures between 363 K and 78 K for the VV polarization configuration. At the highest temperature, 363 K, one can discern two distinct peaks clearly. As we cool the crystal, one can begin to distinguish a shoulder on the red edge of the higher frequency of the two main features. Most importantly, the top left panel of Figure 4 shows the central position of both peaks shift. Researchers observe similar peak shifts in the C=O stretching vibrations of hydrogen bonded pharmaceutical molecules in their solid state [64]. We denote the first peak as corresponding to the vibration $\nu_1$ and the second peak as corresponding to the vibration $\nu_2$.

The next region shown in the top right panel of Figure 9 is approximately 1265 cm$^{-1}$ where we compare several temperatures using the HH polarization configuration. Based on our analysis of the polarization anisotropy in Figure 9, we believe the HH polarization configuration corresponds to polarizing the incident and scattered photon electric fields along the $a$-axis of the TFMBI crystal. We denote this peak as corresponding to the vibration $\nu_3$. The bottom left panel of Figure 9 shows the Raman spectra of TFMBI at several representative temperatures between 363 K and 78 K in the region between 1370 cm$^{-1}$ and 1425 cm$^{-1}$ for the VV polarization configuration. We find a peak centered at 1392 cm$^{-1}$ for our measurement at 363 K shifts upward in effective frequency to over 1402 cm$^{-1}$ upon cooling the sample to 78 K. We denote this peak as corresponding to the vibration $\nu_4$. 
Figure 9: **Top left:** Temperature dependent Raman spectra of a TFMBI single crystal in the VV polarization configuration in the region around 1000 cm\(^{-1}\). **Top right:** Temperature dependent Raman spectra of a TFMBI single crystal in the HH polarization configuration in the region around 1260 cm\(^{-1}\). **Bottom left:** Temperature dependent Raman spectra of a TFMBI single crystal in the VV polarization configuration in the region around 1400 cm\(^{-1}\). **Bottom right:** Temperature dependent Raman spectra of a TFMBI single crystal in the VV polarization configuration in the region around 1550 cm\(^{-1}\).
The final intramolecular region, the bottom right panel of figure 9, shows the Raman spectra of TFMBI measured experimentally for 5 representative temperatures between 363 K and 78 K in the region around 1550 cm$^{-1}$ for the VV polarization configuration. We find the Raman peak within this spectral window shifts from 1542 cm$^{-1}$ to 1551 cm$^{-1}$ upon cooling through these temperatures. Furthermore, we find the shape of the peak changes at 78 K and likely indicates similar changes in lattice strain as the temperature of the $\nu_2$ peak discussed above. We denote this peak as corresponding to the $\nu_5$ vibration. We observe as we cool our sample peak shifts throughout the intramolecular region of our Raman spectra and we seek to explain these shifts.

2.4 RESULTS FROM CRYSTAL17 (DFT)

To gain an understanding of the microscopic behavior of TFMBI we used density functional theory to calculate and assign the vibrational frequencies or eigenvaules. The top left panel of Figure 10 compares the VV-polarized Raman spectrum of crystalline TFMBI measured experimentally around 1000 cm$^{-1}$ at 298 K to the Raman intensity spectrum computed using DFT calculations for excitation and detection polarizations aligned along the $c$-axis of the crystal. This panel shows when we scale the computed frequency axis by 0.955 we find quite good agreement between the computed and measured Raman spectra. In particular, we find both the positions and relative intensities of the computed peaks match their measured counterparts closely.

Furthermore, close inspection of the computed spectrum shows the higher frequency of the two peaks possesses a shoulder similar to that of measured spectra at temperatures below 323 K. The inset in the top left panel of Figure 10 show the eigenvectors for the experimental peak at approximately 1005 cm$^{-1}$ associated with the computed peaks in the spectral comparison. Inspection of the figure inset shows the pyrazine N of each TFMBI molecule moves in a direction
orthogonal to this plane for the higher frequency vibration. In addition, while the carbon atom of the trifluoromethyl group moves to modulate its angle with the pyrrole N of its constituents in the higher frequency vibration, this atom moves to change the C-C bond length with the apical carbon of the imidazole ring for the lower frequency vibration. Despite these differences, the gross atomic motions comprising these eigenvectors correspond to similar types of distortions to both the imidazole and benzene rings of the constituent TFMBI molecules.

The top right panel of Figure 10 is the comparison of the peaks experimentally measured at 298 K around 1260 cm$^{-1}$ to the spectrum calculated with DFT indicates they correspond to ring stretching vibrations. In particular, the dominant motions of the main peak of the spectra correspond to C and N atoms of the benzene and imidazole rings. Furthermore, while the pyrrole N atoms of each TFMBI molecule does not participate in this vibration, the normal mode possess significant motion of its pyrazine N atom. We find these atoms move along the crystal’s $a$-axis nominally, as one expects given the polarization configuration we used to acquire our experimental spectra. We find similar results when analyzing the atomic motions comprising the small peak to the red of the most intense peak of the calculated spectrum.

The bottom left panel of Figure 10 compares the VV-polarized Raman spectra we measured experimentally at 298 K to that found from DFT calculations for excitation and detection polarizations along the $c$-axis of the crystal. We scaled the computed frequency axis by 0.955. Close inspection of this comparison shows the computed spectrum possesses all of the important features found experimentally. Specifically, we find two peaks around 1320 cm$^{-1}$ and a third peak at 1400 cm$^{-1}$ fit almost exactly. Furthermore, the computed spectrum closely resembles the relative intensities of the three peaks found from our experimental measurements. The inset of the bottom left panel of Figure 10 shows the eigenvector corresponding to the highest frequency of the computed
peaks. This image shows carbon atomic motions largely comprise this vibration. In particular, this vibration strongly modulates the length of C-C bond between trifluoromethyl group and apex of imidazole ring. However, unlike the atomic motions comprising $\nu_1$ and $\nu_3$, the N atoms of each constituent TFMBI do not contribute substantially to the motions of $\nu_4$.

The bottom right panel of the Figure 10 compares the VV-polarized Raman spectrum measured experimentally at 298 K to the spectrum computed with DFT for excitation and detection polarizations aligned with the $c$-axis of the crystal. When comparing the ability of DFT to predict the Raman spectra in the regions examined above, inspection of the comparison in the bottom right panel to the other panels finds relatively poorer agreement between experiment and computation. In particular, while there are peaks in the computed spectrum close to those of our measured counterpart, even the 0.955 scaling of the computed frequency axis cannot provide their overlap. Furthermore, the relative intensities of the computed spectrum do not match those of the experimental results. Despite these deficiencies, we note the presence of peaks in the same spectral region indicates the experimental peaks correspond to vibrations of the pristine TFMBI crystalline structure.

2.5 SIGNIFICANT FINDINGS

Our crystallographically based polarization configuration and the DFT calculations show all five of these peaks correspond to vibrations that modulate the polarizability of the material’s unit cell in the predominant direction of its intermolecular hydrogen bonding network, the crystal’s $c$-axis. Based on this coincidence, we seek to determine whether the observed Raman peak shifts result from changes in the microscopic hydrogen bonding structure of TFMBI as dictated by the vibrational Stark effect [52] or from the quartic anharmonic contribution to the interatomic potential
Figure 10: **Top left:** Comparison between the cc-polarized Raman spectrum calculated with DFT (red) and the experimentally measured spectrum at 298 K in the VV polarization configuration (blue). Inset: atomic motions comprising calculated vibrations found at 1053 cm$^{-1}$ (right) from DFT calculations. **Top right:** Comparison between the aa-polarized Raman spectrum calculated with DFT scaled by a factor of 0.955 (red) and the experimentally measured spectrum at 298 K in the HH polarization configuration (blue) Inset: atomic motions comprising a calculated vibration at 1345 cm$^{-1}$. **Bottom left:** Comparison between the cc-polarized Raman spectrum calculated with DFT (red) and the experimentally measured spectrum at 298 K in the VV polarization configuration (blue). Inset: atomic motions comprising a calculated vibration found at 1473 cm$^{-1}$ from DFT calculations. **Bottom right:** Comparison between the cc-polarized Raman spectrum calculated with DFT (red) and the experimentally measured spectrum at 298 K in the VV polarization configuration (blue) Inset: atomic motions comprising a calculated vibration at 1634 cm$^{-1}$. 
To assess the hypothesis that the temperature-driven peak shifts in the Raman spectra of the TFMBI crystal stem from the vibrational Stark effect, we measured the Raman spectra of TFMBI molecules solvated in molecular liquids characterized by different bulk dielectric constants. Several authors have shown Onsager’s proposed connection between the bulk electrostatic properties of molecular liquids and the microscopic reaction field the polarizability constituents of these liquids induce on solvated molecules can be used to show the energy states of particular analyte vibrations obey the Stark effect [85, 86, 87, 52, 53, 54]. Given the very low solubility of TFMBI in non-polar solvents, we were left dissolving this analyte in the following polar solvents: dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetone, methanol, ethanol, and propanol. Our results are shown in figure 11.

The left panel of Figure 11 shows the results of this methodology for the spectral region around 1000 cm\(^{-1}\) and polarized Raman scattering conditions. For clarity, we partition the solution-phase Raman spectra into panels associated with the non-alcoholic (top panel) and alcoholic (bottom panel) solvents. By inspecting the panels of Figure 11 we find that despite a systematic change in the dielectric of the bulk solvent upon changing from DMSO to acetone, we do not observe an associated, deterministic shift of either peak to higher effective frequency. These results suggest the shifts of the peaks corresponding to the \(\nu_1\) and \(\nu_2\) vibrations observed in crystalline TFMBI do not arise due to the vibrational Stark effect.

The right pane of Figure 11 shows the dependence of the polarized Raman spectrum of TFMBI molecules on the solvent dielectric constant in the region near the \(\nu_3\) vibration denoted above (1260 cm\(^{-1}\)). By examining these spectra for the solvents listed above, we find an important difference between the solid and liquid state measurements. In contrast to the Raman spectra of
Figure 11: **Left figure:** Comparison between the polarized Raman spectra of TFMBI molecules around 1000 cm$^{-1}$ in the non-alcoholic solvents DMSO (blue), DMF (red), and acetone (green). Comparison between the Raman spectra of TFMBI molecules around 1000 cm$^{-1}$ in the alcoholic solvents methanol (blue), ethanol, (red), and propanol (green). **Right figure:** comparison between the polarized Raman spectra of TFMBI molecules around 1260 cm$^{-1}$ in the non-alcoholic solvents DMSO (blue), DMF (red), and acetone (green). Comparison between the polarized Raman spectra of TFMBI molecules around 1260 cm$^{-1}$ in the alcoholic solvents methanol (blue), ethanol, (red), and propanol (green).

crystalline TFMBI shown in Figure 10 top right panel, Figure 11 shows the lower frequency feature of in the region around $\nu_3$ possesses a higher intensity than its higher frequency counterpart. So while we do observe peak shifts consistent with deterministic changes of the solvent dielectric constant, we cannot make a firm assignment of solution phase spectrum in the region near $\nu_3$.

Without this assignment we presume for the moment the temperature dependent shifts we observe in Figure 9 do not stem from the vibrational Stark effect and assess the ability of our anharmonic coupling model to predict them.

With our determination that the vibrational Stark effect cannot explain the peak shifts we observe in crystalline TFMBI appropriately, we seek to establish if the anharmonic structural model can provide more fundamental physical insights into the mechanism accounting for our experimen-
tal results. While previous studies outline the theory of the vibrational Stark and bond polarization effects [55], we develop a theoretical model of the anharmonic contributions to the material’s interatomic forces, i.e. structural anharmonicity. For the case of this study, we will presume the vibrations considered above possess dispersion-less frequencies. Given the frequencies and normal modes of the vibrations shown in the experimental results section, we believe this presumption will hold given the ability of similar assumptions to treat electron-phonon coupling in molecular crystals appropriately [88]. Furthermore, we envision these vibrations couple to lower frequency vibrations that also possess dispersion-less energies, the validity of which we assess below.

The hydrogen bonding interaction between the molecules of crystalline TFMBI manifest from the crystal structure and vibrational Raman spectrum of the N-H stretching modes acts to modulate the electronic density at each lattice site. If strong enough, then this modulation of the electronic density should imprint itself on the properties of the vibrations corresponding to the molecular constituents of the material, such as the vibrational frequency. To test this intuitive connection between changes in the electronic density and vibrational properties as a function of changing the hydrogen bonding network within the material, we expand the interatomic potential energy between the material’s atoms in terms of the eigenvectors of the dynamical matrix, \( \{Q_i\} \), as [58],

\[
U(Q) \approx U(0) + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 U(Q)}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j + \frac{1}{3!} \sum_{i,j,k} \left( \frac{\partial^3 U(Q)}{\partial Q_i \partial Q_j \partial Q_k} \right)_0 Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} \left( \frac{\partial^4 U(Q)}{\partial Q_i \partial Q_j \partial Q_k \partial Q_l} \right)_0 Q_i Q_j Q_k Q_l + \ldots,
\]

since the first order term in the expansion must be zero due to the definition of equilibrium. We presume the equilibrium geometry of the crystal corresponds to the case when \( Q = 0 \) to write Eq.
2.1 in the form shown.

The quadratic term gives rise to the harmonic contribution therefore we can ignore this term. The cubic and quartic terms gives rise to the anharmonicity. In particular the cubic term represents the phonon self energy, which renormalizes both the real and imaginary parts of the vibrational frequency. This term leads to changes in the line shape in the Raman spectra substantially [59, 60]. The quartic term however, only shifts the vibrational frequencies without affecting the peak line shape when one considers first time order time independent perturbative corrections to the vibrational energy. Therefore, we only consider the quartic terms in Eq 2.1 to explain the anharmonicity of aromatic ring vibrations present in the Raman spectra of TFMBI. We develop an anharmonic model based on Maradudin and Fein. See appendix A. [57]

Our model is based off of equation 2.2 and 2.3 where $\Gamma_1$ is the Lorentzian width of the peak centered at $\omega'$, $\omega$ is the difference between the incident and scattered photons, and $A$ describes the modulation of the unit cell dipole moment by the atomic motion along the vibrational normal coordinates, $(\partial \mu_{eg}/\partial Q_i)_0$, and the detuning of the incidence and scattered light fields from the electronic transitions of the material.

$$\omega' = \frac{1}{\hbar} \left( E_1^{(0)} + E_1^{(1)} - E_0^{(0)} - E_0^{(1)} \right) = \omega^{(0)} - 2\frac{g_{12}}{\hbar}(2n_2 + 1), \quad (2.2)$$

$$\frac{d\sigma}{d\omega} \propto \frac{|A|^2 \Gamma_1}{(\omega - \omega')^2 + \Gamma_1^2}, \quad (2.3)$$
where $\omega^{(0)}$ is the harmonic frequency of the fundamental vibrational excitation we find from DFT calculations.

Specifically, we test the ability of Eq. 2.2 and 2.3 to account for the shift of each peak we observed in our experimental measurements through nonlinear least squares fitting. We modeled the average occupation of coupling mode with, $n_2$, using the Bose factor, $1/[\exp(h\omega_c/k_B T) - 1]$, where $\omega_c$ is the coupling mode frequency. We approach the fitting procedure in two ways. First, we use the harmonic frequency found from DFT calculations as $\omega^{(0)}$ for each respective vibration. We then find values of the interaction energy, $g_{12}$ and coupling frequency, $\omega_c$, that best reproduce the temperature dependent trends of the positions of the $\nu_3$, $\nu_4$, and $\nu_5$ vibrations of crystalline TFMBI.

The presence of at least two discontinuities in the temperature dependent positions of the $\nu_1$ and $\nu_2$ modes impeded our ability to assess if the anharmonic coupling model explains their behavior. For the case of the $\nu_4$ mode, we fit the peak position trend for temperatures equal to or above 198 K and below 198 K separately to account for the structural transition we propose occurs near 173 K. In addition, we preclude the position of the $\nu_5$ mode we find at 78 K from the fitting routine given its odd shape.

Second, we allowed the fitting routine to find the best value for the harmonic frequency and then used that value to re-fit the measured trend to equation 2.2. This algorithm provided more precise estimates of both $g_{12}$ and $\omega_c$ than if we let the routine fit all three parameters of Eq. 2.2 and allows us to test for temperature dependence interaction energies, as discussed below. Figure 12 shows the results of this analysis and Table 3 in appendix A details the parameters we extract from the fits of the measured peak positions to Eq. 2.2 for each structural phase consistent with the $\nu_4$ trend. Figure 12 shows our anharmonic model results.
Figure 12: Comparison of the temperature dependence of measured peak positions to Eq. 2.2 for the $\nu_1$ (top left), $\nu_2$ (top right), $\nu_3$ (bottom left), and $\nu_4$ (bottom right) vibrations denoted in the main text.
Inspection of Figure 12 indicates the ability of the anharmonic structural model detailed above to explain the positions of the $\nu_3$, $\nu_4$, and $\nu_5$ vibrations of crystalline TFMBI depends critically on the value of the harmonic frequency used in the fitting routine. While our quartic anharmonic model can explain the gross behaviors of the peak positions as a function of TFMBI sample temperature when we use the harmonic frequencies established by our DFT calculations, the fitting does not capture the correct temperature dependent variation in the peak position. For instance, all the panels of Figure 7 show when we use the $\omega^{(0)}$ values established from ab initio calculations the model overestimates the peak shift we measure in the higher range of temperatures systematically for every vibration, but then underestimates the vibrational frequency in the lower temperature range.

In contrast to these results, the fitting routine predicts smaller values of $\omega^{(0)}$ for all three of the modes, which substantially improve the fit of the model to the experimental temperature dependent trend of peak positions over those using the harmonic frequencies we find through DFT calculations. Specifically, we find the fits neither overestimate the anharmonic shift in the higher temperature range nor underestimate this shift at lower temperatures. Moreover, we find by changing the value of the harmonic frequency also changes the values of $g_{12}$ and $\omega_c/2\pi c$ predicted by the model. In particular, we find both of these values decrease as we reduce the harmonic frequency used in Eq. 2.2. We find the most dramatic effect for the case of the $\nu_5$ mode. When we replace the $\omega_5^{(0)}$ predicted from DFT calculations with the value we find from our fitting routine $g_{12}$ reduces by a factor of 20 and the $\omega_c$ reduces by more than a factor of 4.

We rationalize these changes by considering the magnitude of the shift necessary to explain the experimental data. When we consider a harmonic frequency far from that which we measure experimentally, the model balances between a large value of $g_{12}$ to reproduce the shifted peak po-
position at low temperatures and high frequency coupling mode to reproduce the rapid shift in higher temperature range. When we consider a smaller harmonic frequency, the model needs a smaller value of $g_{12}$ to shift the peak appropriately at low temperatures and can accommodate a smaller coupling mode frequency to explain the shifts at high temperatures. This lower coupling mode frequency also better reproduces the temperature dependence due to finite average occupations at the lowest temperatures we consider in our experimental studies. Based on this analysis, we conclude our DFT calculations produce overly large harmonic vibrational frequencies and one should be able to use the peak shifts due to structural anharmonicity as an additional test of the harmonic frequencies found from ab initio electronic structure calculations. Furthermore, the good agreement between the model fit and measured peak positions indicates quartic anharmonic interaction energy $g_{12}$ does not depend on temperature, which we assumed in our derivation of Eq. 2.2.
CHAPTER 3 2D HYBRID ORGANIC-INORGANIC PEROVSKITES


3.1 BACKGROUND AND PREVIOUS LITERATURE: COUPLING OF LAYERS

Hybrid organic-inorganic perovskites (HOIPs) have been shown to be promising for optoelectronic applications [89, 90, 91, 92, 93]. The prototypical and the most studied HOIP is the methylammonium lead halide with a completely interconnected three-dimensional (3D) inorganic struc-
ture, which attracted much attention due to their low cost [94], ease of synthesis [95], and excellent electrical and optical properties [96, 97]. However, their relatively poor stability in air [98, 99, 100] under realistic operational conditions hinders future development of these 3D hybrid perovskites at the device level. In contrast, as an emerging class of materials, layered 2D HOIPs feature much better environmental stability [15, 16] while maintaining the flexibility in tuning their electronic properties [101, 102, 103] as well as the desired performance in applications such as photovoltaics [17] and light emitting diodes [18].

In 2D HOIPs, the basic building blocks are inorganic layers that often consist of lead and halogen atoms and organic layers that often consist of long molecules with ammonium functional groups [104]. The layered structure gives rise to distinct physics from 3D HOIPs, such as generally stronger exciton binding energies [105]. Understanding these phenomena requires a complete characterization of the coupling between the inorganic and organic layers [106] and how the coupling depends on the atomistic details in the crystal structure [107], which is currently missing for 2D HOIPs.

Studies of the vibrational properties in HOIPs yield valuable information on the interplay between the inorganic framework and the organic molecule to provide physical insights into their dynamical interactions [108, 109, 106, 107, 110]. For this purpose, both infrared (IR) and Raman spectroscopic studies have shown that the behavior of the organic cation depends on microscopic organic-inorganic interactions [107, 111, 112, 106]. For 3D HOIPs, several studies indicated the facets of the coupled organic-inorganic structural dynamics [113], including the role of dynamic disorder [114], polar fluctuations, [115] and static dielectric environments [107, 116]. Additionally, Ref. [117] focused on the dynamic structure-property relationships and found that the Raman activity of the methylammonium molecule is very sensitive to structural distortions of the inor-
ganic framework. For 2D HOIPs, using temperature- and polarization-dependent measurements, Ref. [118] found strong evidence of anisotropy in the vibrational bands in phenethylammonium lead bromide, and attributed the anisotropy to the orientation of the phenethyl ring with respect to the inorganic lattice framework. Given the importance played by the ammonium functional group in the coupling between the inorganic and organic layers in 2D HOIPs, carefully characterizing its vibrational properties is central to understanding the interactions between the inorganic lead-halide framework and the organic spacer cations.

3.2 RESEARCH METHODS

Preparation of 2D Hybrid Organic-Inorganic Perovskites The starting chemicals were purchased from Sigma-Aldrich and synthesized without further purification. We prepared our perovskite crystal structures using the methods previously reported [106, 119, 120, 121].

Specifically, we synthesized (HA)$_2$PbI$_4$ by dissolving 74 mg of PbI$_2$ in 3 mL of HI in a beaker and transferred gently into a test tube using a syringe. To the test tube containing the PbI$_2$ in HI solution, we gently added 3 mL of methanol. Due to the difference in densities, an interface was formed between the solvents. We then gently added 1 mL hexylamine to the tube using a syringe. We covered the test tube with thin foil. Orange plate-like crystals started forming within 24 hrs. We let more crystals form until 5 days before filtering the crystals under suction. The orange crystals were washed with cold diethyl ether, dried in the oven at 60 °C for 24 hrs.

(HA)$_2$PbBr$_4$ was synthesized by dissolving 58.5 mg of PbBr$_2$ in 3 mL of 48% HBr in a beaker and transferred gently into a test tube using a syringe. To the test tube containing the PbBr$_2$ in HBr solution, 3 mL of methanol was gently added using a syringe. Hexylamine (1 mL) was then gently added to the test tube and the test tube was covered with thin foil. White plate-like crystals started
forming within 24 hrs. We let more crystals form until 5 days before filtering the crystals under suction. The white crystals were washed with cold diethyl ether, dried in the oven at 60 °C for 24 hrs.

To synthesize \((\text{BA})_2\text{PbI}_4\), we dissolved and heat to 130 °C, 1.16 mmol lead iodide in 2 mL HI solution in one beaker. We neutralized 2.32 mmol butylamine with 3 mL HI in a second beaker. The neutralized butylamine solution was then added to the lead iodide solution while heating and stirring for approximately 20 minutes under a dry nitrogen atmosphere. The solution was then cooled to room temperature and orange crystals formed. The crystallization was completed in an ice bath for 2 hrs and filtered crystals were washed and dried in a vacuum oven at 60 °C for 24 hrs.

We synthesized \((\text{BNA})_2\text{PbI}_4\) by following similar method used in synthesizing \((\text{HA})_2\text{PbI}_4\). We dissolved 74 mg of \(\text{PbI}_2\) in 3 mL of 57% HI in a beaker, followed by transferring the solution gently into a test tube using a syringe. To the test tube containing the \(\text{PbI}_2\) in HI solution, 3 mL of methanol was gently placed on the lead iodide solution. We gently added 0.5 mL benzylamine to the test tube and covered the test tube with thin foil. Orange plate-like crystals started forming within 24 hrs. We let more crystals form until 4 days before filtering the crystals by suction. The orange crystals were washed with cold diethyl ether and dried in the oven at 60 °C for 24 hrs.

**Raman Scattering Measurements**  We collected our experimental Raman scattering spectra with a Horiba XploRA PLUS Raman micro-spectrometer. The excitation laser light was set at 785 nm and dispersed in a 0.3 m monochromator using a 1800 g/mm diffraction grating. Our instrument is setup in a 180° backscattering arrangement and allows measurements dependent on both the incidence and scattered electric field polarizations. We choose the direction of the incident laser polarization which is either parallel (VV, vertical) or perpendicular (HV, horizontal)
to the polarization of the detected scattered electric field. A Linkam THMS600 liquid-nitrogen temperature probe controlled the temperature of each sample with a precision of ±0.5 K. We allowed the sample to settle for approximately 5 min at each desired temperature before acquiring the spectra.

While the first-principles calculations of the vibrational spectra of our 2D HOIP samples necessarily assume a temperature of 0 K, we present Raman spectra acquired at 77 K for all the samples except (BA)$_2$PbI$_4$. We compare our computational results for (BA)$_2$PbI$_4$ to Raman measurements undertaken at room temperature because this material undergoes an orthorhombic-orthorhombic structural transition near 260 K upon cooling. This difference in the temperature of the computed and measured materials could introduce ambiguity in our comparison of the experimentally measured and calculated vibrational frequencies. However, we justify our comparison of the vibrational spectra at different temperatures based on established anharmonic mechanisms that couple the dynamics of the inorganic and organic sub-lattices of 2D HOIPs [106].

Unlike many of the other intramolecular vibrations of 2D HOIPs, the ammonium bending vibration undergoes temperature-dependent shifts of its peak position. Unlike the shifts of the delocalized phonon frequencies that stem from the contraction and expansion of the lattice with changes in the thermal environment, our previous study [106] shows the shifts of the ammonium bending vibration stem from anharmonic coupling to low-frequency phonon modes. These anharmonic couplings depend entirely on the thermal population of the lattice phonons through their Bose-Einstein factors. For the phonon frequencies we found coupled to the ammonium bending vibration in our 2D HOIP samples, we expect only their ground states are appreciably populated at 77 K. Therefore, any further cooling of these samples would not cause a change in the phonon state population or the anharmonic coupling necessary to shift the peak frequency of the ammo-
nium bending vibration meaningfully from the positions we measure at 77 K.

**First-Principles Calculations** We employ first-principles calculations to assign experimental peaks in Raman spectra as specific vibrational modes and to understand the effect of the crystal structure in modulating the vibrational properties of the organic molecular cation. We first optimize the structures of each material using density functional theory (DFT) [122, 123], and subsequently calculate their vibrational properties based on DFPT [124] as implemented in the Quantum ESPRESSO [125] package. The Perdew-Zunger form of local density approximation (LDA) [126, 127] was used for all geometry optimization and DFPT calculations. The pseudopotentials are adapted from Refs. [128, 129].

For the geometry optimization of (HA)$_2$PbI$_4$, (BA)$_2$PbI$_4$, and (BNA)$_2$PbI$_4$, we use the crystal structure resolved from X-ray diffraction experiments [130] as the initial guess. During the optimization, all lattice parameters and atomic coordinates are relaxed while keeping the lattice symmetry to be the experimentally determined one [monoclinic for (HA)$_2$PbI$_4$ and orthorhombic for (BA)$_2$PbI$_4$ and (BNA)$_2$PbI$_4$]. For (HA)$_2$PbBr$_4$, we have not found experimentally determined lattice structure, so we assume it has the same space group as (HA)$_2$PbI$_4$ and use the (HA)$_2$PbI$_4$ structure with all iodine atoms replaced by bromine as the initial guess. For (HA)$_2$PbI$_4$ and (HA)$_2$PbBr$_4$, we have checked that a k-mesh of $5 \times 5 \times 3$ and a kinetic energy cutoff of 100 Ry lead to a convergence in total energies of the unit cell within 5 meV/atom, and so we use a cutoff of 130 Ry in the variable-cell relaxation to mitigate the Pulay stress. For (BA)$_2$PbI$_4$ and (BNA)$_2$PbI$_4$, a k-mesh of $5 \times 5 \times 2$ and a cutoff of 130 Ry were used. The optimization is considered complete when all forces are below 0.05 eV/Å and the pressure of the cell is below 0.5 kbar.

After the optimized structures are obtained, we proceed with the self-consistent calculation of
the electronic structure using a kinetic energy cutoff of 100 Ry and the same k-mesh as above, before the vibrational calculations using DFPT. Since the Raman experiments only measure Γ-centered modes [131], we constrain our DFPT calculations of the phonon normal modes and Raman activities [132] to the Γ point only. The crystal acoustic sum rule is applied in the diagonalization of the dynamical matrix, and we have checked that it correctly yields three zero-frequency modes. Using a slightly tailored version of the code, we output each component of the Raman activities, \(|\partial \alpha_{ij}/\partial Q_\nu|^2\), where \(\alpha_{ij}\) is the polarizability tensor with \(i, j = x, y, \) or \(z\) and \(Q_\nu\) denotes the normal-mode coordinate.

### 3.3 RESULTS FROM COUPLING OF LAYERS

We study three different Pb-halide perovskite-like semiconductors which are hexyl-ammonium lead iodide, benzyl-ammonium lead iodide and butyl-ammonium lead iodide. Fig. 13(a) shows the optimized unit cell of \((HA)_2PbI_4\), with a base-centered monoclinic crystal structure. Two lead atoms occupy the corners and the face centers of the (001) plane. The lead and iodine atoms form corner-sharing octahedra in the (001) plane, with four \(HA^+\) cations filled between two adjacent layers of Pb-I octahedra. The structure of \((HA)_2PbBr_4\) is very similar to that of \((HA)_2PbI_4\), with bromine atoms replacing iodine atoms and slightly different lattice parameters. Fig. 13(b)(c) show the optimized unit cells of \((BA)_2PbI_4\) and \((BNA)_2PbI_4\), with a face-centered orthorhombic crystal structure. One lead atom occupies the corners and three lead atoms occupy the face centers. The lead and iodine atoms form corner-sharing octahedra in both the (001) and the (002) planes. Four organic spacer cations are filled between each two adjacent layers of Pb-I octahedra and there are overall eight organic cations in the unit cell. In Appendix B, table 4 we compared the crystallographic parameters from experiment and our DFT calculations. We find our LDA-
Figure 13: The optimized crystal structure of (a) \((HA)_2\text{PbI}_4\), (b) \((BA)_2\text{PbI}_4\), and (c) \((BNA)_2\text{PbI}_4\). The corner-sharing \(\text{PbI}_6\) octahedra are shown. The structure of \((HA)_2\text{PbBr}_4\) is similar to (a) with iodide atoms replaced by bromide. Color code: C - yellow; H - cyan; N - blue; Pb - magenta; I - green. This figure is rendered using VESTA [133].

Based calculations underestimate lattice parameters by about 3%-5% and the crystal volume by about 10%, which is consistent with the typical performance of LDA in bond lengths and lattice parameters [134].

**Hexyl-Ammonium Lead Iodide**  For \((HA)_2\text{PbI}_4\), we compare the experimentally measured Raman intensities in both VV and HV polarizations and calculated \(xx\), \(yy\), and \(xy\) contributions to the Raman intensities in Figure 14. In this work, for all calculated Raman intensities, we apply a Lorentzian broadening to each mode with a 3 cm\(^{-1}\) half width at half maximum in the figures, and use atomic units (a.u.) throughout, i.e., Bohr\(^4\)/amu with amu the atomic mass unit. One can see that the VV (HV) qualitatively agrees with the \(xx\) and \(yy\) (xy) contributions to the Raman intensity. Due to the large intensities of the low-frequency modes seen in experiment, we use dif-
Figure 14: Comparison between measured and calculated Raman spectra for (HA)$_2$PbI$_4$. (a) The experimentally measured Raman intensities, in HV (red) and VV (green) polarizations at 78 K. Due to the large intensities of the low-frequency modes, we use different scales in the vertical axis below (left axis) and above (right axis) 400 cm$^{-1}$. (b) The $xx$ contribution to the calculated Raman intensity, scaled up by 3 times. (c) The $yy$ contribution to the calculated Raman intensity, scaled up by 2 times. (d) The $xy$ contribution to the calculated Raman intensity.

For all materials, the nature of all phonon modes can be categorized into the following: the modes below 500 cm$^{-1}$ are combinations of the translations/vibrations of the lead-halogen framework and the librations/hindered rotations of the organic molecules. The modes between 500 cm$^{-1}$ and 1650 cm$^{-1}$ are the bending modes of the organic molecule. Specifically, all the bending modes of the ammonium group are between 1400 cm$^{-1}$ and 1600 cm$^{-1}$, which we focus on in
this paper. No modes are within the 1650-2850 cm\(^{-1}\) range. Modes above 2850 cm\(^{-1}\) are the H-X (X = C, N) bond stretching modes of the organic molecule, which we cannot detect with our experimental apparatus.

We note from Figure 14(a) that the strongest Raman intensity of molecular vibrational modes appears in two frequency ranges: 800-1000 cm\(^{-1}\) and 1400-1600 cm\(^{-1}\). The former mainly consists of the bending modes of the carbon backbone of the organic molecule sandwiched between the inorganic layers. Given the complexity of the molecular backbone structure and the variety of organic molecules used in 2D HOIPs, such modes are unlikely representative across a broad range of organic molecules in various 2D HOIPs. Furthermore, since the molecular backbone is relatively far away from the lead-halogen framework, their bending modes could not sensitively reflect the effect of the lead-halogen framework. On the other hand, the latter region, 1400-1600 cm\(^{-1}\), mainly consists of the bending modes of the -NH\(_3\) group in the organic molecule, which is both ubiquitous in many 2D HOIPs and close to the inorganic layer of the crystal. Since our goal is to study the coupling between the inorganic and organic layers, we focus on the 1400-1600 cm\(^{-1}\) in this work.

Figure 15 shows the measured and calculated Raman activities from DFPT, for (HA)\(_2\)PbI\(_4\) between 1400 cm\(^{-1}\) and 1600 cm\(^{-1}\). Figure 15(a) includes the experimental Raman spectra of both polarizations VV (red) and HV (green) at 78 K. We observe a major peak at 1484.7 cm\(^{-1}\), and two minor ones at 1553.5 cm\(^{-1}\) and 1562.9 cm\(^{-1}\), respectively. In Figures 15(b)(c)(d), we show several contributions to the calculated Raman intensity: \(xx\) in (b), \(yy\) in (c), and \(xy\) in (d). To make the range in the vertical axes the same for (b)(c)(d), we have scaled up the values in (b) by a factor of 10 and (c) by a factor of 5. From our symmetry analysis above, Figures 15(b)(c) correspond to the VV measurement and Figure 15(d) corresponds to the HV measurement.
In the 1400-1600 cm$^{-1}$ range, there are overall 28 phonon modes with 14 of them Raman active. We labeled each peak to provide a direct comparison to our DFT calculation. Our results are summarized in table 5 in Appendix B.

Figure 16 shows the normal-mode eigenvectors of all modes that are included in Figures 15(b)(c)(d). One can see that the two modes in each group in Table 5 in the Appendix B consist of approximately the same vibrational patterns in all four molecules, and are only different in their symmetry over the unit cell of the crystal. We note that there are six modes that are primarily localized on the -NH$_3$ group and correspond to the ammonium bending modes, which are the last three rows in Table 5 and the last six modes in Figure 16. The two strongest intensities in Figure 15(d) - one at 1449.8 cm$^{-1}$ (peak 13) and one at 1536.4 cm$^{-1}$ (peak 15) - are among these six ammonium bending modes, which suggests that such -NH$_3$ bending modes are useful experimental
Figure 16: A schematic view of all (HA)$_2$PbI$_4$ normal-mode eigenvectors that are included in Figures 15(b)(c)(d). The red arrows depict the direction and magnitude of the vibrational movements for each atom. The peak number in Figure 15, frequency, and symmetry for each mode are also shown. This figure is rendered using XCrySDen [135].

We carry out the same analysis for the other three materials. For (HA)$_2$PbBr$_4$, Figure 17(a) shows the experimental Raman spectra, and Figures 17(b)(c)(d) show the three contributions to the calculated Raman intensities: $xx$ in (b), $yy$ in (c), and $xy$ in (d). We label each peak in Figures 17(b)(c)(d), and show the values of the frequencies and each orientation-dependent contributions to the Raman intensities in Appendix B Table 6, and the schematic view of the normal-mode eigenvectors in Appendix B Figure 40. There are again six Raman-active modes localized on the -NH$_3$ group, which are the last three rows in Table 6 in Appendix B and the last six panels in Figure 40 in Appendix B. From DFPT calculations, the largest Raman intensities are from a mode at 1463.7 cm$^{-1}$ and at 1553.8 cm$^{-1}$, both of which are ammonium bending modes.
Figure 17: The Raman activities of (HA)$_2$PbBr$_4$ between 1400 cm$^{-1}$ and 1600 cm$^{-1}$. (a) Measured Raman intensities in HV (green) and VV (red) polarizations. (b) The $xx$ contribution to the calculated Raman intensity, scaled up by 4 times. (c) The $yy$ contribution to the calculated Raman intensity, scaled up by 2 times. (d) The $xy$ contribution to the calculated Raman intensity. Peak numbers are shown to facilitate references in Table 6 and Figure 39. (appendix B)

**BENZYL AND BUTYL AMMONIUM LEAD IODIDE**

For (BA)$_2$PbI$_4$ [(BNA)$_2$PbI$_4$], Figure 18 (Figure 19) shows the experimental Raman spectra in (a) and the three contributions to the calculated Raman intensities in (b)(c)(d). We label each peak in Figure 18 (Figure 19), and show the values of the frequencies and each orientation-dependent contributions to the Raman intensities in Table 7 (Table 8) in appendix B, and the schematic view of the normal-mode eigenvectors in Figure 41 (Figure 42) in appendix B. In these two materials, we recognize that the modes within 1400-1600 cm$^{-1}$ range can be divided into groups with 8 modes in each group having similar frequencies, consistent with the 8 molecules in the unit cell. Among the 8 modes in each group, 4 are Raman active, with $A_g$, $B_{1g}$, $B_{2g}$, and $B_{3g}$ symmetries, respectively, as can be seen in Tables 7 and 8 (Appendix B). There are 12 Raman-active modes localized on the -NH$_3$ group, which are shown in the last three rows of Table 7 (appendix B) for (BA)$_2$PbI$_4$ [the second row and the last
two rows of Table 8 (Appendix B) for $(BNA)_2PbI_4$. The calculated largest Raman intensities are from modes at $1451.4$ cm$^{-1}$ and $1540.1$ cm$^{-1}$ for $(BA)_2PbI_4$ [1441.3 cm$^{-1}$ and 1535.8 cm$^{-1}$ for $(BNA)_2PbI_4$], all of which are ammonium bending modes.

Figure 18: The Raman activities of $(BA)_2PbI_4$ between $1400$ cm$^{-1}$ and $1600$ cm$^{-1}$. (a) Measured Raman intensities in HV (green) and VV (red) polarizations. (b) The $xx$ contribution to the calculated Raman intensity, scaled up by 3 times. (c) The $yy$ contribution to the calculated Raman intensity, scaled up by 8 times. (d) The $xy$ contribution to the calculated Raman intensity. Peak numbers are shown to facilitate references in Table 7 and Figure 41. (appendix B)

**Different Density Functionals and Quantitative Comparison with Experiment**

In Figure 15, we notice the apparent discrepancy (about 30 cm$^{-1}$) between experimental and computational results in the frequencies of the predominant peaks. We attribute this to the intrinsic error of the LDA functional, which is known to underestimate the phonon frequencies [136]. Unambiguous assignment of experimental peaks requires a correction to the errors made by the underlying density functional used in the DFPT calculations. To this end, we follow and generalize the strategy employed in Ref. [137]. The basic assumption is that LDA-based DFPT yields reasonably accurate
Figure 19: The Raman activities of \((\text{BNA})_2\text{PbI}_4\) between 1400 cm\(^{-1}\) and 1600 cm\(^{-1}\). (a) Measured Raman intensities in HV (green) and VV (red) polarizations. (b) The \(xx\) contribution to the calculated Raman intensity, scaled up by 5 times. (c) The \(yy\) contribution to the calculated Raman intensity, scaled up by 4 times. (d) The \(xy\) contribution to the calculated Raman intensity. Peak numbers are shown to facilitate references in Table 8 and Figure 42. (appendix B)

eigenvectors (normal modes) of the dynamical matrix, but not eigenvalues (phonon frequencies).

The remedy is the following: we first compute total energies using a different functional - preferably one that is more accurate than LDA - for a series of geometries along a 1D potential energy curve where the atoms are displaced based on a specific normal mode of interest (which is from LDA-based DFPT), and then calculate the phonon frequencies corresponding to the new functional via a quadratic fitting of the 1D potential energy curve. This frozen-phonon approach is based on the harmonic approximation, and requires that the atomic displacements are small. Before a new functional is used, we use LDA to recalculate the frequency of the normal mode of interest using the frozen-phonon approach, and compare the result against that of the LDA-based DFPT. In the ideal case, we expect that LDA in the frozen-phonon approach yields the same frequency as DFPT for the same mode, and the frequency computed using the more accurate func-
tional in the frozen-phonon approach is then supposed to be a better prediction to the experimental measurement than LDA-based DFPT.

In the frozen-phonon approach, the displacement of an atom \( I \) along the spatial direction \( \alpha \) (= \( x, y, \) or \( z \)) in the normal mode \( \nu \) is [137, 131]

\[
\Delta_{I\alpha,\nu} = \sqrt{\frac{M_0}{M_I}} e_{I\alpha,\nu} \delta_\nu, \tag{3.1}
\]

where \( \delta_\nu \) is the magnitude of the displacement along the normal-mode coordinate and is small to ensure the harmonic approximation, \( M_0 \) is the reduced mass, \( M_I \) is the mass of atom \( I \), and \( e_{I\alpha,\nu} \) is the normalized eigenvector of the dynamical matrix for mode \( \nu \). After the total energies of a series of displaced structures \( E(\delta_\nu) \) are calculated using the new functional, the corrected frequency for mode \( \nu \) can be calculated using

\[
\omega_\nu^2 = \frac{1}{M_0} \frac{d^2 E(\delta_\nu)}{d\delta_\nu^2}. \tag{3.2}
\]

Figure 20: 1D potential energy curves along the normal-mode coordinates of (HA)\(_2\)PbI\(_4\), for (a) peak 13 in Figure 15 (1449.8 cm\(^{-1}\) using LDA-based DFPT); (b) peaks 4 and 10 in Figure 15 (1500.6 cm\(^{-1}\) using LDA-based DFPT); and (c) peak 15 in Figure 15 (1536.4 cm\(^{-1}\) using LDA-based DFPT). LDA (blue), PBE (red), and vdw-DF-cx (green) functionals are used. Solid lines represent the quadratic fitting used to calculate the phonon frequency from each functional. The energy of the equilibrium structure is set to be zero in all curves.

Figure 20 shows our results using the frozen-phonon approach, for three representative modes of (HA)\(_2\)PbI\(_4\). We consider the last three groups of modes in Table 5, which are the ammonium
bending modes. We choose the mode with the higher Raman intensity in each group: 1449.8 cm$^{-1}$ (peak 13 in Figure 15), 1500.6 cm$^{-1}$ (peaks 4 and 10 in Figure 15), and 1536.4 cm$^{-1}$ (peak 15 in Figure 15). In the frozen-phonon approach, we displace the atoms along the normal-mode coordinates up to 0.3 Å from the equilibrium structure, at an interval of 0.05 Å. To be specific, for each mode $\nu$ we examine, the $3N$ ($N$=number of atoms) coordinates of the structure are displaced according to Eq. (3.1), where $\delta_\nu = 0.05, 0.1, \cdots , 0.3$ Å. A quadratic form is used to fit the 1D energy curves in Figure 20. We first use LDA in the frozen-phonon approach to verify that it could reasonably reproduce the DFPT results (see discussions below). We then proceed to use two other functionals, the Perdew-Burke-Ernzerhof (PBE) [138] and the vdw-DF-cx [139] to evaluate the phonon frequencies. Similar calculations are performed for high Raman intensity modes in other materials, and we show the corresponding 1D potential energy curves in Appendix B figures 43, 44 and 45.

<table>
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<tr>
<th>Peak Number</th>
<th>Experiment</th>
<th>DFPT (LDA)</th>
<th>LDA</th>
<th>PBE</th>
<th>vdw-DF-cx</th>
<th>frozen phonon scaled</th>
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<tr>
<td>(HA)$_2$PbI$_4$ (Figure 15)</td>
<td>4 &amp; 10</td>
<td>1484.7</td>
<td>1449.8</td>
<td>1449.8</td>
<td>1503.7</td>
<td>1487.2</td>
</tr>
<tr>
<td>(HA)$_2$PbBr$_4$ (Figure 17)</td>
<td>15</td>
<td>1496.3</td>
<td>1463.7</td>
<td>1427.5</td>
<td>1478.8</td>
<td>1461.1</td>
</tr>
<tr>
<td>(BA)$_2$PbI$_4$ (Figure 18)</td>
<td>16</td>
<td>1479.0</td>
<td>1451.3</td>
<td>1418.7</td>
<td>1464.4</td>
<td>1447.8</td>
</tr>
<tr>
<td>(BNA)$_2$PbI$_4$ (Figure 19)</td>
<td>16</td>
<td>1552.7</td>
<td>1535.8</td>
<td>1526.6</td>
<td>1577.0</td>
<td>1562.4</td>
</tr>
</tbody>
</table>

Table 1: Comparison between selected normal modes from experiments, LDA-based DFPT, and the frozen-phonon approach using different functionals. Peak numbers refer to labelled peaks in relevant figures for each material and correspond to modes with the strongest Raman coefficients in the 1400-1600 cm$^{-1}$ range. Experimental frequencies are the peak positions in panel (a) of each relevant figure. “Scaled” means using the ratio of vdw-DF-cx and LDA frequencies in the frozen-phonon approach to scale the LDA-based DFPT frequency. All frequencies are in cm$^{-1}$.

Table 1 summarizes the frozen-phonon results for all materials. Except for peak 15 of (HA)$_2$PbBr$_4$, peak 15 of (BA)$_2$PbI$_4$, and peak 13 of (BNA)$_2$PbI$_4$, LDA in the frozen-phonon ap-
approach does reproduce the phonon frequencies directly calculated using DFPT within 10 cm\(^{-1}\), as expected. For such cases, LDA (both within the DFPT and the frozen-phonon formalisms) underestimates the experimental frequencies by about 3\%, while PBE overestimates the experimental frequencies by about 1\%, as expected. [140] The state-of-the-art van der Waals density functional, vdw-DF-cx [139], quantitatively agrees with experimental measurements. It is however unclear to us why the situation is different for the aforementioned three modes, where the discrepancy between LDA in the frozen-phonon approach and DFPT can be as large as 40 cm\(^{-1}\). We suspect that the shallow potential energy surface of the organic cations in such materials [141], and/or the breakdown of the harmonic approximation for some modes [106] may be the possible reason for this discrepancy. We defer a thorough investigation of this issue to a future work.

Here, we take a rather practical approach, generalizing Ref. [137]. We consider the ratio of frequencies calculated from vdw-DF-cx and LDA in the frozen-phonon approach. This ratio characterizes the difference in the curvatures of the 1D potential energy curves (i.e., interatomic force constants) calculated by the two functionals. We think that this ratio reflects the difference of these two functionals in describing phonon properties and therefore use this ratio to scale the frequencies calculated from LDA-based DFPT. The results are shown in the last column of Table 1. One can see that this strategy yields quantitative agreement between experimental and computational results, enabling us to unambiguously assign experimental peaks with specific normal modes.

Overall, the frozen-phonon approach based on DFPT normal-mode eigenvectors could reliably and efficiently correct intrinsic errors of the underlying functional used in the DFPT calculation, LDA in this case. When an advanced functional is used, such as the vdw-DF-cx for the 2D HOIP here, this approach leads to quantitative agreement between the vibrational frequencies found in experiment and computation. Given the complexity of the 2D HOIP unit cells, such agreement is
of paramount significance in accurately assigning each peak in the experimental Raman spectra.

Now we have an understanding of the discrepancy between experiment and calculation we next took a further look at the ammonium bending modes. As we see in Figures 15 and 16, the ammonium bending modes dominate the Raman intensity in the 1400-1600 cm$^{-1}$ range. For (HA)$_2$PbI$_4$, there are six Raman-active ammonium bending modes in the crystal, which can be divided into three groups, with two modes in each group sharing the same vibrational character of the -NH$_3$ functional group, as we have discussed in Figure 16 and Table 5. Given their strong localization on the -NH$_3$ group of the molecule (the displacement of the carbon backbone is negligible in such modes, see Figure 16), these three groups of bending modes are reminiscent of the three bending modes in an isolated NH$_3$ molecule, where one symmetric bending (A$_1$ symmetry) and two degenerate asymmetric bending (E symmetry) modes are present. The differences between the -NH$_3$ bending modes in the crystal and those in an isolated NH$_3$ molecule are due to two factors: (i) The carbon backbone of the organic cation (HA$^+$) causes a blueshift in the frequencies and breaks the degeneracy of the two asymmetric bending modes found in an isolated NH$_3$ molecule; (ii) the lattice framework of the crystal that consists of lead and halogen atoms further alters the frequencies of the isolated HA$^+$ cation to those of the crystal. We show below that the crystal effect can be well-described by a PbI$_3$ fragment placed next to an isolated HA$^+$ cation.

To this end, we consider an isolated HA$^+$ cation in the gas phase, whose atomic coordinates are the same as one HA$^+$ cation in the optimized (HA)$_2$PbI$_4$ crystal. The HA$^+$ cation is modeled in a large simulation cell of 30 Å $\times$ 30 Å $\times$ 40 Å with a k-mesh of 1$\times$1$\times$1. Moreover, we consider another system, where in addition to the HA$^+$, we place a PbI$_3$ fragment nearby, whose atomic coordinates and relative orientations with the HA$^+$ molecule are the same as those in the optimized (HA)$_2$PbI$_4$ crystal. The goal here is to find and use the smallest possible lead-iodine structure that
Figure 21: The three groups of Raman-active ammonium bending modes in the (HA)$_2$PbI$_4$ crystal (where there are two modes in each group), compared to the corresponding modes in an isolated HA$^+$ cation and a charge-neutral system that consists of a HA$^+$ cation placed next to a PbI$_3^-$ fragment. All frequencies are from LDA-based DFPT. (a) Symmetric ammonium bending. (b) Asymmetric ammonium bending. (c) Another asymmetric ammonium bending, with different atomic displacement patterns than (b). This figure is rendered using XCrySDen [135].

could modulate the modes of an isolated HA$^+$ cation into those of the (HA)$_2$PbI$_4$ crystal. Since lead and iodine atoms form PbI$_6$ octahedra in the crystal, we choose the three iodine atoms forming the “octant” in which the -NH$_3$ functional group is located. We have checked that in the crystal, the four HA$^+$ cations are in similar chemical environments in terms of their relative orientations with a neighboring PbI$_3$ fragment. The resulting “HA$^+$PbI$_3^-$” unit is charge neutral and is again modeled in a large simulation cell of 30 Å×30 Å×40 Å with a k-mesh of 1×1×1. We then perform LDA-based DFPT calculations for the isolated HA$^+$ cation and the HA$^+$PbI$_3^-$ system and compare their ammonium bending modes with those in (HA)$_2$PbI$_4$ crystal. Similar analysis is carried out for the other three crystals studied in this work.
Figure 21 shows the comparison of normal-mode eigenvectors of the three ammonium bending modes between the (HA)$_2$PbI$_4$ crystal, an isolated HA$^+$ cation, and the HA$^+$PbI$_3^-$ system. Figure 21(a) shows the symmetric bending mode and Figure 21(b)(c) show the two asymmetric bending modes. The cases for other materials are shown in Appendix B: (HA)$_2$PbBr$_4$ in Figure 46, (BA)$_2$PbI$_4$ in Figure 47, and (BNA)$_2$PbI$_4$ in Figure 48. In Figure 21, one can see that for each particular mode, the atomic displacement patterns within the -NH$_3$ functional group are similar among the three systems. We note that strictly speaking, each normal mode consists of vibrational motions of all atoms and the modes shown in Figure 21 are only those “largely localized” on the -NH$_3$ functional group. The quantitative difference in frequencies between the (HA)$_2$PbI$_4$ crystal and the isolated HA$^+$ molecule can be well explained by the neighboring PbI$_3^-$ fragment. Our finding is consistent with Ref. [108], where the PbI$_3^-$ is used to explain the difference in the torsional modes within the 200-400 cm$^{-1}$ range, between an isolated methyl-ammonium cation and the 3D methyl-ammonium lead iodide.

To physically explain the effect of the PbI$_3^-$ fragment in modulating the vibrational frequencies of the isolated HA$^+$, we perform the following analysis. First, we use the aforementioned frozen-phonon approach and the LDA functional to recompute the frequencies of the last two (almost degenerate) HA$^+$ modes in Figure 21. The resulting frequencies are 1582.1 cm$^{-1}$ and 1577.1 cm$^{-1}$, respectively, in good agreement with the LDA-DFPT results (1579.6 cm$^{-1}$ and 1589.8 cm$^{-1}$, see Figure 21). Next, using these HA$^+$ normal modes as the displacement patterns, we compute the frequencies of the HA$^+$PbI$_3^-$ using the frozen-phonon approach, assuming Pb and I atoms do not move. In other words, the HA$^+$ in HA$^+$PbI$_3^-$ is displaced in exactly the same way as the isolated HA$^+$, with a fixed PbI$_3^-$ fragment placed nearby. The resulting frequencies are 1507.9 cm$^{-1}$ and 1526.8 cm$^{-1}$, respectively, again in good agreement with the LDA-DFPT results for HA$^+$PbI$_3^-$.
The 1D potential energy curves for the frozen-phonon calculations of the HA$^+$ and the HA$^+$PbI$_3^-$ are shown in Figure 22. Such results indicate that, the presence of PbI$_3^-$ near the HA$^+$ distorts the potential energy surface of the latter, effectively altering the frequencies of the -NH$_3$ localized modes. We note in passing that because the coordinates of both the HA$^+$ and the HA$^+$PbI$_3^-$ are fixed to be those in the relaxed (HA)$_2$PbI$_4$ crystal rather than the individually relaxed species in the gas phase, the energy minima of the two species do not coincide, as we see in Figure 22. We have checked that the phonon frequencies of the fully relaxed HA$^+$ and HA$^+$PbI$_3^-$ in the gas phase are very similar (within 10 cm$^{-1}$) to the results reported here.

Additionally, besides PbI$_3^-$, we have also checked explicitly that a neutral PbI$_2$ fragment placed next to the HA$^+$ cation could not quantitatively explain all the frequency differences: it leads to 1439.7 cm$^{-1}$, 1505.7 cm$^{-1}$, and 1567.7 cm$^{-1}$, respectively, for the three modes shown in Figure

![Figure 22: 1D potential energy curves along the normal-mode coordinates of an isolated HA$^+$, for (a) the asymmetric -NH$_3$ bending mode as shown in Figure 21(b); and (b) another asymmetric -NH$_3$ bending mode as shown in Figure 21(c). Blue dots are calculations of the isolated HA$^+$. Red dots are calculations of the HA$^+$PbI$_3^-$ structure, which is displaced according to the corresponding HA$^+$ normal modes (assuming Pb and I atoms do not move). Solid lines represent the quadratic fitting used to calculate the phonon frequencies. The energy of the non-distorted structure - with the same coordinates as those in the relaxed (HA)$_2$PbI$_4$ crystal - is set to be zero in both systems.](image-url)
Although the first two modes are similar to those of the crystal, the frequency of the last asymmetric -NH$_3$ bending mode is apparently off the mark. Moreover, we could rule out the vibrational Stark effect as a possible explanation of the frequency difference between HA$^+$ and the (HA)$_2$PbI$_4$ crystal: the frequency shift under a static electric field of a reasonable intensity [on the order of 0.01 a.u., as determined by the electrostatic potential difference between an isolated HA$^+$ and the (HA)$_2$PbI$_4$ crystal] is only about 10 cm$^{-1}$, much smaller than the 50-100 cm$^{-1}$ that we see in Fig. 21.

<table>
<thead>
<tr>
<th></th>
<th>Symmetric -NH$_3$ bending</th>
<th>Asymmetric -NH$_3$ bending</th>
<th>Asymmetric -NH$_3$ bending</th>
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<td>(HA)$_2$PbI$_4$</td>
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<td></td>
<td></td>
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<td>HA$^+$</td>
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</tr>
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<td>1500.6 A$_g$</td>
<td>1536.4 B$_g$</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
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</tr>
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<tr>
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Table 2: Comparison of the three -NH$_3$ bending modes in an isolated cation, an isolated cation next to a nearby PbX$_3^-$ (X=Br or I) fragment, and the crystal, for (HA)$_2$PbI$_4$, (HA)$_2$PbBr$_4$, (BA)$_2$PbI$_4$, and (BNA)$_2$PbI$_4$. All frequencies are calculated from LDA-based DFPT and in cm$^{-1}$.

In Table 2, we summarize the results for all materials. We compare the frequencies of the three ammonium bending modes, for the isolated organic cation, the cation+PbX$_3^-$ (X = Br or I), and the crystal. For all cases, a PbX$_3^-$ placed next to the organic cation successfully explains the
difference in frequencies between an isolated organic cation and the 2D HOIP crystal. The only exception is the symmetric \(-\text{NH}_3\) bending mode in \((\text{BNA})_2\text{PbI}_4\), where a blueshift of the frequency from the isolated cation is found for the crystal, while the use of the \(\text{PbI}_3^-\) yields a redshift. As we showed in Figure 22 for \((\text{HA})_2\text{PbI}_4\), the difference between an isolated cation and the crystal could be physically attributed to the distortion of the potential energy surface of the organic cation by the neighboring \(\text{PbX}_3^-\), which is local in the crystal. Therefore, these modes listed in Table 2 not only feature the strongest Raman intensities in the 1400-1600 cm\(^{-1}\) range, but also are sensitive to the local chemical environment around the \(-\text{NH}_3\) functional group (recall that a \(\text{PbI}_2\) fragment placed next to the \(\text{HA}^+\) yields very different frequencies). As a consequence, we think that these ammonium bending modes could serve as a useful experimental probe to the microscopic structure of the lead-halogen octahedra that form the lattice framework of the 2D HOIP crystal. For instance, given the sensitivity of the Raman properties of these ammonium bending modes on the neighboring \(\text{PbX}_3^-\) structure, such modes might be able to provide useful information on possible lead or halogen defects in the crystal that give rise to light emission below the materials' optical gaps [142, 143, 144, 119, 145, 146, 147], which is a point to be scrutinized in future work.

### 3.4 SIGNIFICANT FINDINGS

We used a combination of Raman spectroscopy in the backscattering geometry and first-principles calculations to characterize the Raman spectra of four similarly structured two-dimensional hybrid organic-inorganic perovskites, \((\text{HA})_2\text{PbI}_4\), \((\text{HA})_2\text{PbBr}_4\), \((\text{BA})_2\text{PbI}_4\), and \((\text{BNA})_2\text{PbI}_4\). We focused on the 1400-1600 cm\(^{-1}\) range where the ammonium bending modes dominate the Raman intensity. We first obtained normal-mode eigenvectors from DFPT using LDA, and then performed frozen-phonon calculations using the vdw-DF-cx functional for a series
of geometries with atoms displaced along the DFPT normal-mode eigenvectors. We found that this strategy leads to quantitative agreement between experiment and computation, which helped us in unambiguously assigning experimental Raman peaks as normal modes of the crystal. We discussed the relationship between the ammonium bending modes in the periodic crystal and in the isolated organic cation, and found that a PbX$_3^-$ ($X = \text{Br or I}$) fragment placed next to the organic cation could successfully explain the crystal effect on the ammonium bending modes.

3.5 BACKGROUND AND PREVIOUS LITERATURE: DEFECTS

As we discovered the importance of understanding the coupling of the layers we next investigated the role defects play in these lead halide perovskites. The use of longer cation amines alleviates the instability of the bulk 3D perovskites [100, 148]. In recent years, 2D perovskites have been seen to emit photoluminescence across the visible spectrum, white light. This makes these materials a desirable candidate for the next generation of solid-state phosphors [149]. However, the mechanism driving the observed white light emission remains unclear. There are two widely studied mechanisms that researchers conclude could be responsible for the photoluminescence features observed. Defects and self trapped excitons are the two studied mechanisms. [150, 151]

We explored the effect of localized defects. The presence of defects inside the bandgaps of these hybrid perovskite-like semiconductors can enable researchers to control the PL features observed. The defects could act as radiative centers from which single photons can be emitted. Booker et al studied the role iodide related defects affect the density of states in hexyl-ammonium lead iodide. Their results suggest that stable interstitial iodide defects may be responsible for white light emission seen 2D lead halide perovskites [19]. It has also been seen that iodide ions are the most mobile in hybrid materials [152]. This empowers the further investigation of iodide related
defects and the role they play.

3.6 RESEARCH METHOD

To establish the nature of the electronic states participating in narrowband light emission from HA$_2$PbI$_4$, we employ first-principles density functional theory (DFT) [122, 123] to compute the band structure and projected density of states (PDOS) for the perovskite of interest, hexylammonium lead iodide. Specifically, we model four systems: (a) the pristine structure; (b) a defective structure with a pair of correlated I$^-$ and H$^+$ vacancies while keeping the system charge neutral; (c) a defective structure with a neutral I vacancy; and (d) a defective structure with a charged I$^-$ vacancy. In all defective structures, we remove the I or I$^-$ from the equatorial position, and in (b) we additionally remove its nearest H$^+$ from the ammonium group in the molecule. All the calculations employ the Quantum ESPRESSO package [125] and the optimized norm-conserving Vanderbilt (ONCV) pseudo-potentials [129].

We start by relaxing the lattice parameters and the atomic positions in the pristine structure using the Perdew-Burke-Ernzerhof (PBE) functional [72] and a $4 \times 4 \times 2$ k-mesh, where we use the crystal structure resolved from the X-ray diffraction experiments as the initial guess and fix the symmetry of the crystal to be monoclinic. The resulting lattice parameters are: $a = 8.930 \, \text{Å}$, $b = 9.018 \, \text{Å}$, $c = 17.083 \, \text{Å}$, $\alpha = 90^\circ$, $\beta = 94.945^\circ$, and $\gamma = 90^\circ$. These values are within 5% of the experimental values and our previous results [153] relaxed using the local density approximation. We found a kinetic energy cutoff of 80 Ry leads to a convergence in energy within 5 meV/atom, therefore used a cutoff of 100 Ry in the variable-cell relaxation to mitigate the Pulay stress.

We consider three supercell sizes when we create the defective structures: $1 \times 1 \times 1$, $2 \times 2 \times 1$, and $3 \times 3 \times 1$, where we create one defect site per supercell to examine the change in electronic
structure as we gradually lower the density of the defect. We found that the $2 \times 2 \times 1$ supercell yields almost the same results as the $3 \times 3 \times 1$ supercell, and hence focus on the $2 \times 2 \times 1$ supercell size in this work. Additionally, we found that extending the supercell along the $c$ direction does not change the results either. Furthermore, because we do not find a significant change in the lattice parameters experimentally when we introduce defects into the structure, we fix the lattice parameters of the defective structures as those of the pristine structure, and only relax the atomic positions, with a kinetic energy cutoff of 80 Ry. For PBE calculations, we use a $2 \times 2 \times 2$ k-mesh for the $2 \times 2 \times 1$ supercell and a $1 \times 1 \times 2$ k-mesh for the $3 \times 3 \times 1$ supercell.

### 3.7 RESULTS FROM MODELED DEFECTS

Figure 23 shows the temperature dependence of the subgap PL of our HA$_2$PbI$_4$ samples in three separate spectral regions. In the highest energy region, we find the intensity of a complex structure of peaks reduces as we cool this sample.

![Figure 23: Temperature dependence of the PL spectra of defective HA$_2$PbI$_4$](image)

We want to investigate the mechanism driving these PL features we observe. We propose the narrowband features result from the presence of several states whose energies lie above that of the top of the material’s valence band. To understand the chemical identity of the defective site that
give rise to the trapped charges in our samples, we modeled the electronic structure of a \(2 \times 2 \times 1\) supercell containing an iodide vacancy in an equatorial position within an octahedral layer and an associated \(H^+\) vacancy on an adjacent \(HA^{2+}\) cation using periodic plane-wave DFT methods with the Perdew-Burke-Ernzerhof (PBE) functional [72], as described in Methods.

Figure 24 shows the comparison of the defective and pristine material’s electronic band structures, this structural model produces a localized mid-gap electronic state nearly 0.8 eV above the energy of the valence band maximum at the \(\Gamma\)-point of the Brillouin zone. We infer the localized nature of this electronic state from the fact that the mid-gap band is dispersionless. Similar calculations carried out on structural models containing apical and equatorial \(I^-\) vacancies without the correlated \(H^+\) vacancy did not produce similar electronic states within the material’s otherwise pristine band gap. We note that a quantitative determination of the energetics of the bound excitons would require many-body perturbation theory such as the Bethe-Salpeter equation, which is prohibitively expensive given the size of the supercell we consider here.

We calculate projected density of states (PDOS) for both pristine and defective structures to assess which atoms within the modeled supercell contribute to the mid-gap defect state as shown in Figure 25. The PDOS plot provides a further interpretation of the band structure plot. Where we are now looking at the charge build up of the energy states, specifically the orbitals of the atoms. We find at the top of the VB in the pristine \(HA_2PbI_4\), a small peak stems from p-orbitals of the \(I^-\). When we remove the equatorial I atom in our structural model of defective \(HA_2PbI_4\), we find those states become expectedly removed. In addition, we find the localized defect state stems largely from the p orbitals of the N atom in the hexyl amine adjacent to the \(H^+\) vacancy. As a consistency check, we calculated the PDOS of a \(2 \times 2 \times 1\) supercell of \(HA_2PbI_4\) using the hybrid Hyed-Scuseria-Ernzerhof (HSE) functional [154].
3.8 SIGNIFICANT FINDINGS

We considered the formation of defects in self-assembled, perovskite-like quantum well samples capable of emitting light spectra significantly more narrow than those assigned to self-trapped electronic excitations previously. With our fundamental understanding of the coupling between the layers we modeled defects that correlate directly to the coupling of the layers (NH$_3$). We find a combination of an iodide vacancy and the nearest hydrogen atom vacancy predicts a mid-gap state in the band gap of our material. Periodic plane-wave DFT calculations indicate that the defect states participating in the radiative relaxation of the trapped charge stems predominantly from p-orbitals of N atoms. This assignment helps us to explain both the activation of different narrowband PL signals by distinct vibrations of the molecular cation and the competition between the light emission intensity between a bound exciton and its associated electron.
Figure 25: Comparison of the PDOS onto the orbitals of different atoms of HA$_2$PbI$_4$ between the pristine (left) and defective (right) structures showing the non-dispersive state in the defective material stems mostly from the p orbitals of molecular N atoms. Both structures are fully relaxed. Inset: expanded view of the PDOS of the defective structure between energies of 0.25 and 1.1 eV above the pristine material’s VBM.
CHAPTER 4 METAL ORGANIC FRAMEWORKS


4.1 BACKGROUND AND PREVIOUS LITERATURE

Improvement of fuel energy storage and the fuel refining process is centrally focused on the separation of light hydrocarbons. Fractional distillation [155] is one widely used method for hydrocarbon separation. This approach however, is energy-consuming and can be inefficient for mixtures with very similar boiling points. Metal-organic frameworks (MOFs) [156, 157, 158] have attracted much attention in many areas, such as carbon capture [159, 160, 161], catalysis [162, 163], precursor in synthesis [164, 165, 166], hydrogen storage [167, 168], and gas separation [169, 170, 171, 172, 173, 174, 175]. MOFs feature great tunability in pore size and shape [26, 27], owing to the rich chemical space that one can explore by combining different linker molecules with different metal centers [176, 177], and are thus excellent candidates for the adsorptive separation of gas molecules such as small hydrocarbons [28, 29, 30].

Most MOFs feature open metal sites, i.e., coordinatively unsaturated metal atoms [178], which tend to interact strongly with π orbitals of guest adsorbates. Such a binding preference leads to the separation of CO₂, C₂H₂, and CH₄ using MOF-74 [179], O₂/N₂ separation using different MOFs [180, 181], methanol/acetone separation using M-BTC [182], flue gas separation [183] using MOF-74, among others. In the context of hydrocarbon separation, the same concept explains
the separation of olefins from paraffins [184, 185, 186, 187, 188]. However, for MOFs with open metal sites, it is reported that there could be a rapid loss in the activity after adsorbates are bound to MOFs, resulting in the poisoning of the metal center and a reduction of the uptake capacities of adsorbates [189, 183]. To overcome this issue, MOFs without open metal sites have been developed, with prominent examples being NOTT-300-Al [190, 191], MFM-300 series with various metal centers [192, 193, 194, 195, 196], and MIL-47-V [197, 198]. However, a fundamental understanding of the binding and gas separation mechanism at the atomistic level in such MOFs, as well as a comparison between different MOFs without open metal sites are still missing. To this end, insights from accurate first-principles calculations are needed.

### 4.2 STRUCTURES STUDIED

![Figure 26: Structures of the four MOFs studied in this work: (a) MFM-300-V(III); (b) MFM-300-V(IV); (c) MIL-47-V(III); and (d) MIL-47-V(IV). Black boxes denote the simulation cells. (e) Zoomed-in view of the bridging hydroxyl group (μ₂-OH) connecting two V(III) atoms in (a) and (c). (f) Zoomed-in view of the bridging oxo group (μ₂-O) between two V(IV) atoms in (b) and (d). (g) the organic linker used in (a) and (b). (h) the organic linker used in (c) and (d). Color Code: C-brown; H-light pink; O-red; V-magenta. All figures in this paper are rendered using VESTA [199].](image)

Figures 26(a-d) display all MOF structures studied in this work, where we show one simulation cell for each MOF. MFM-300-V(IV) [MIL-47-V(IV)] is the oxidized counterpart of MFM-300-
Figure 26(e) highlights the local binding geometry near two neighboring vanadium atoms in both MFM-300-V\(^{\text{III}}\) and MIL-47-V\(^{\text{III}}\) structures, where one can see an -OH group bridging two vanadium atoms, i.e., a \(\mu_2\)-OH. It also shows that the coordination chemistry in that region is the same for both the MFM-300 family and the MIL-47 family. Each vanadium atom is coordinated with four organic linkers and two bridging -OH groups, and every adjacent pair of vanadium atoms share three functional groups bridging them: two carboxylate groups in the organic linker and one \(\mu_2\)-OH. Figure 26(f) highlights the local binding geometry near two neighboring vanadium atoms in both MFM-300-V\(^{\text{IV}}\) and MIL-47-V\(^{\text{IV}}\), where one can see an oxo group bridging two vanadium atoms (i.e., a \(\mu_2\)-O atom) instead of the \(\mu_2\)-OH, which is the only structural difference between V\(^{\text{III}}\) and V\(^{\text{IV}}\) MOFs of the same family. Figure 26(g) shows the organic linker used in the MFM-300-V family, the biphenyl-3,3',5,5'-tetracarboxylic acid. MIL-47-V\(^{\text{III}}\) and MIL-47-V\(^{\text{IV}}\) possess the so-called “wine-rack” motif [200] and use terephthalic acid as the organic linker, shown in Figure 26(h). The differences in structure between the MFM-300 and the MIL-47 families as well as between the V\(^{\text{III}}\) and V\(^{\text{IV}}\) MOFs of the same family lead to differences in the binding with unsaturated hydrocarbons.

4.3 RESEARCH METHODS

We start our geometry optimization using experimentally determined structures and atomic coordinates whenever available [201, 202]. All calculations employ the optimized norm-conserving Vanderbilt (ONCV) pseudopotentials [203, 204] and the vdW-DF-cx functional [205] as implemented in the Quantum ESPRESSO package [206], with periodic boundary conditions along all directions. We note that a functional capturing van der Waals dispersion is required to accurately describe the binding between guest molecules and the MOF, as we have explicitly checked that the
Perdew-Burke-Ernzerhof (PBE) functional leads to binding energies that are one order of magnitude smaller than those calculated using vdw-DF-cx, as expected. For MFM-300, the convergence study shows that a kinetic energy cutoff of 70 Ry and the Γ-point sampling converge the total energy per atom within 5 meV. Therefore, we use a kinetic energy cutoff of 90 Ry (to mitigate the Pulay stress) for variable-cell relaxations of these MOFs as well as the related molecule@MOF composite systems, where we fix the symmetry of the structure to be the experimentally determined tetragonal [201]. The relaxation is considered complete when all forces are below 0.05 eV/Å and the pressure is below 0.5 kbar for the simulation cell. In another convergence study, we have checked that a 120 Ry kinetic energy cutoff and a force criterion of 0.02 eV/Å lead to the same binding energy (within 0.1 kJ/mol) as the parameters used in this work.

For the MIL-47 family, we use the same kinetic energy cutoff as above and a k-mesh of $1 \times 1 \times 2$ for their variable-cell relaxations, where we fix the symmetry of the structure to be orthorhombic, which is the experimentally determined symmetry for MIL-47-V(IV) [197, 207]. For MIL-47-V(III), the structure can be either monoclinic [197] or orthorhombic [198] depending on the preparation of the sample. We consider the orthorhombic phase here to facilitate a direct comparison computationally. Additionally, there is one complication regarding the relaxations of the molecule@MIL-47 systems: Ref. [208] and others showed that the “wine-rack” type of MOFs could “breathe” (a significant change in lattice parameters) when guest molecules are adsorbed within the pores. However, Refs. [209, 210] reported the rigidity of MIL-47 upon adsorption of small hydrocarbons under typical gas pressures, where its lattice parameters are nearly unchanged. Here, we follow these works and fix the lattice parameters in all molecule@MIL-47 systems as those of the corresponding MIL-47 [either V(III) or (IV)], and relax all atomic coordinates.

The binding energies are calculated as following: $B.E. = E(MOF) + nE(molecule) -$
$E_{\text{molecule@MOF}}$, where $n$ is the number of molecules adsorbed in the specific MOF. $E_{\text{molecule@MOF}}$ is the total energy of the fully relaxed composite system where multiple guest molecules are adsorbed within the pores of the MOF (variable-cell relaxations for the MFM-300 family and fixed-cell relaxations for the MIL-47 family); $E_{\text{MOF}}$ is the total energy of the fully relaxed MOF structure (variable-cell relaxation for each one); $E_{\text{molecule}}$ is the total energy of one fully relaxed hydrocarbon molecule placed in a $20\text{Å} \times 20\text{Å} \times 20\text{Å}$ simulation box, which we calculate using a kinetic energy cutoff that is consistent with the corresponding MOF and molecule@MOF systems.

Lastly, we comment that all our conclusions above are built upon binding energies calculated using the vdW-DF-cx functional. Materials featuring localized $d$-electrons are known to be problematic for standard local and semi-local functionals. To justify that our choice of the functional is indeed suitable for this class of material, we have computed binding energies for $\text{C}_2\text{H}_2@\text{MFM-300-V^{(III)}}$ and $\text{C}_2\text{H}_2@\text{MFM-300-V^{(IV)}}$ at both binding sites using vdW-DF-cx0 [211], the hybrid version of vdW-DF-cx. The binding energies vary within 5%-10%, with the trend unchanged. Such results indicate that our vdW-DF-cx results are reliable as far as the trends of binding energies are concerned.

### 4.4 RESULTS FROM DFT

For each MOF, we consider two binding sites for the guest hydrocarbon molecules. There are two distinct binding sites within the MFM-300 family adopted from Ref. [201]. Figure 27 shows the two sites we study. At site 1, the molecules are located close to the bridging -OH groups between two vanadium atoms. At site 2, the molecules are located close to the organic linkers. Figure 27 (a) and (b) correspond to the MFM-300 site 1 and site 2. Figure 27 (c) and (d) are
sites 1 and 2 for MIL-47. The difference between MFM-300 and MIL-47 arises from the linker. Therefore, differences in binding with guest molecules will provide insight into their structure-property relationships.

Figure 27: Molecular adsorption sites within the pores of the MOFs. Here, we use the $V^{(III)}$ MOFs and the $C_2H_2$ molecule as an example to show different adsorption sites. (a) MFM-300-$V^{(III)}$ binding site 1; (b) MFM-300-$V^{(III)}$ binding site 2; (c) MIL-47-$V^{(III)}$ binding site 1; (d) MIL-47-$V^{(III)}$ binding site 2. In (a) and (c), the guest molecules are located close to the bridging -OH groups. In (b) and (d), the guest molecules are located close to the organic linkers.

We consider a 1:1 ratio between the number of light hydrocarbons and the number of binding sites. As shown in Figure 27, for MFM-300, we consider 8 molecules per unit cell with 4 molecules in each pore, due to the presence of 4 possible binding site 1 positions and another 4 possible binding site 2 positions per pore. Experimentally, this loading corresponds to a gas pressure of 0.3-0.4 bar for the MFM-300 family with $C_2H_n$ ($n = 2, 4, 6$) [201]. For MIL-47, there are 4 (8) possible binding site 1 (site 2) positions in each unit cell. Furthermore, we consider all molecules within the pores occupying equivalent sites, i.e., all at site 1 or all at site 2. In reality, both sites
could be simultaneously occupied especially at high gas pressure, and the competition between the
two sites can be described by a dual-site Langmuir model [212, 213, 214].

Figure 28: The most stable binding conformation of C\textsubscript{2}H\textsubscript{4} at binding site 1 in the four MOF
structures: (a) MFM-300-V\textsuperscript{(III)}; (b) MFM-300-V\textsuperscript{(IV)}; (c) MIL-47-V\textsuperscript{(III)}; and (d) MIL-47-V\textsuperscript{(IV)}.
Only one molecule and the closest atoms near the binding site are shown to highlight the local
binding environment.

The binding energies for the V\textsuperscript{(III)} and V\textsuperscript{(IV)} MOFs are almost identical at site 2, for both the
MFM-300 and the MIL-47 families. This is because the linker is similar where the binding site
is located. The situation for site 1 is different. We show in Figure 28 the local binding geometry
near the bridging -OH or -O group for the most stable conformation, with pertinent bond dis-
tances marked. For MIL-47-V\textsuperscript{(III)} [Figure 28(c)], the C\textsubscript{2}H\textsubscript{4} plane is perpendicular to the bridging
-OH connecting the two vanadium atom in a “side-on” conformation. The distance between the
hydrogen atom in the $\mu_2$-OH and the two carbon atoms in C\textsubscript{2}H\textsubscript{4} is about 2.5 Å, which is consis-
tent with the typical bonding distance between an -OH group and a carbon-carbon double bond
[215, 216, 217], with the interaction being electrostatic between the electronegative $\pi$ electrons in the carbon-carbon double bond and the electropositive hydrogen in the -OH. The orientation, i.e., carbon $p_z$ orbital aligned with the -OH, also supports such a conclusion, making the binding directional.

For MIL-47-V$^{(IV)}$ [Figure 28(d)], due to the absence of the hydrogen in the bridging group, the C$_2$H$_4$ binds to the $\mu_2$-O using one hydrogen atom in a “head-on” conformation, forming weak C-H···O hydrogen bond, whose binding is also directional. The distance between the hydrogen and the oxygen is 2.7 Å, consistent with typical C-H···O bond [218]. During our relaxation, we found other local minima where the C$_2$H$_4$ rotates around the C-H···O, with similar binding energies (37-38 kJ/mol compared to the most stable 39.0 kJ/mol in Figure 28(d)). As a comparison, the binding energy with MIL-47-V$^{(III)}$ in Figure 28(c) is 47.9 kJ/mol, suggesting that the C-H···O hydrogen bonding in C$_2$H$_4$@MIL-47-V$^{(IV)}$ is weaker than the OH-$\pi$ interaction in C$_2$H$_4$@MIL-47-V$^{(III)}$.

![Figure 29](image-url)  
**Figure 29:** Secondary binding conformation of C$_2$H$_4$ at (a) site 1 of MFM-300-V$^{(III)}$ and (b) site 1 of MFM-300-V$^{(IV)}$. These conformations lead to slightly lower binding energies than those shown in Figure 28. Only one molecule and the closest atoms near the binding site are shown to highlight the local binding environment.

We find differences in the MFM-300 family. Figure 28(a) shows the binding conformation at
site 1 of MFM-300-V(III), where C$_2$H$_4$ does not bind to the bridging -OH using its $\pi$ electrons as in MIL-47-V(III) [Figure 28(c)], but rather, stay much further away from the MOF, with the distance between the hydrogen atom on the bridging -OH and the carbon atoms within C$_2$H$_4$ around 4 Å. This length is greater than typical H-$\pi$ bonding distance and the sum of the vdW radii of hydrogen and carbon atoms, suggesting that the H-$\pi$ interaction may not be the dominating binding mechanism. During our relaxations, we have found other local minima, such as the one shown in Figure 29(a) that is similar to the “side-on” binding with MIL-47-V(III). However, even in this conformation, the distance between the hydrogen atom on the bridging -OH and the carbon atoms within C$_2$H$_4$ is still about 4 Å, unlike the case of MIL-47-V(III). Furthermore, it yields an even lower binding energy (43.6 kJ/mol) compared to the one reported in Figure 28(a) (44.8 kJ/mol).

Note that this long distance between the C$_2$H$_4$ molecule and the MOF does match results from the NPD experiment [201], where the OH-$\pi$ distance is reported to be 3.74 Å.

To understand the nature of the binding of C$_2$H$_4$ at site 1 of MFM-300-V(III) [Figure 28(a)], we plot in Figure 30(a) the change of total charge density upon binding, i.e., $\Delta \rho = \rho(\text{molecule@MOF}) - \rho(\text{MOF}) - \rho(\text{molecule})$. $\rho(\text{molecule@MOF})$ is the charge density of the composite system, $\rho(\text{MOF})$ is the charge density of the MOF alone, and $\rho(\text{molecule})$ is the charge density of all the molecules. All these quantities are calculated using the same atomic positions and simulation cell of the relaxed molecule@MOF system, so no effects of the geometry change is taken into account. Blue (yellow) blobs indicate positive (negative) $\Delta \rho$, i.e., electron charge accumulation (depletion) upon binding. From this figure, one can see that although the molecule is located at site 1, the bridging -OH groups only play a marginal role in the binding. Rather, the main binding mechanism is the interaction between the C$_2$H$_4$ and part of the side chains in the MOF - perhaps via a $\pi - \pi$ interaction - similar to the case of site 2 binding. It explains why the
binding energy is not significantly larger than that of site 2 for this MOF (44.8 kJ/mol at site 1 and 43.1 kJ/mol at site 2).

![Figure 30](image)

Figure 30: The charge density difference upon binding, $\Delta \rho$, for C$_2$H$_4$ at (a) site 1 of MFM-300-V$^{(III)}$ and (b) site 1 of MFM-300-V$^{(IV)}$. Blue (yellow) color indicates electron charge accumulation (depletion) upon binding. The same isosurface value is used for both panels.

For MFM-300-V$^{(IV)}$ [Figure 28(b)], the binding conformation is similar to that of MIL-47-V$^{(IV)}$ [Figure 28(d)], where the C$_2$H$_4$ binds to the MOF using one hydrogen atom in a “head-on” conformation. However, the distance between the hydrogen atom on C$_2$H$_4$ and the bridging -O atom on the MOF is 3.2 Å, about 0.5 Å larger than that in MIL-47-V$^{(IV)}$. This distance of 3.2 Å is also larger than the typical bonding distance in a weak C-H···O hydrogen bond [218, 219, 220].

A secondary binding conformation is shown in Figure 29(b), with slightly lower binding energy [40.9 kJ/mol compared to 43.0 kJ/mol in Figure 28(b)]. To understand the binding mechanism in Figure 28(b), we again plot $\Delta \rho$, in Figure 30(b). Similar to Figure 30(a), the C$_2$H$_4$ mainly interacts with the side chains, explaining the fact that the binding energy at site 1 (43.0 kJ/mol) is almost identical to that at site 2 (43.1 kJ/mol).

In line with the discussion of the C$_2$H$_4$ binding, we discuss both the binding energies and binding conformations when C$_2$H$_2$ is adsorbed in the pores of the four MOFs. The overall trend is
similar to that of \( \text{C}_2\text{H}_4 \): First, for the same family, either MFM-300 or MIL-47, the binding energies at site 2 of both the \( \text{V}^{(\text{III})} \) MOF and the \( \text{V}^{(\text{IV})} \) MOF are similar. Second, the binding energy at site 1 of the \( \text{V}^{(\text{III})} \) MOF is significantly larger than the \( \text{V}^{(\text{IV})} \) counterpart, due to the directional binding between the bridging -OH present in the \( \text{V}^{(\text{III})} \) MOF and the carbon-carbon triple bond. Third, for MFM-300-\( \text{V}^{(\text{IV})} \), the binding energy at site 1 is similar to that at site 2, while for MIL-47-\( \text{V}^{(\text{IV})} \), the binding energy at site 1 is slightly larger than that at site 2. Below we elaborate on the second and third points, particularly focusing on the difference between \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \).

Figure 31 highlights the most stable binding conformations of \( \text{C}_2\text{H}_2 \) at binding site 1 in the four MOF structures studied in this work, where we list the distances between the adsorbate molecule and the MOF. In MIL-47-\( \text{V}^{(\text{III})} \) [Figure 31(c)], the \( \text{C}_2\text{H}_2 \) and the bridging -OH are approximately in the same plane, with the O-H bond perpendicular to the linear \( \text{C}_2\text{H}_2 \) molecule. This conformation suggests that the MOF binds \( \text{C}_2\text{H}_2 \) via a H-\( \pi \) interaction, similar to the situation of \( \text{C}_2\text{H}_4 \). The distances between the hydrogen atom in the -OH and the carbon atoms in the triple bond are 2.4 Å, slightly shorter than the H-\( \pi \) distance with a carbon-carbon double bond [215]. The binding situation for MIL-47-\( \text{V}^{(\text{IV})} \) is also similar to that of \( \text{C}_2\text{H}_4 \)@MIL-47-\( \text{V}^{(\text{IV})} \) [Figure 28(d)], where the hydrocarbon molecule binds to the MOF via a weak “head-on” C-H-\( \cdots \)O hydrogen bond. Due to the smaller steric hindrance in the hydrocarbon, \( \text{C}_2\text{H}_2 \) binds closer (2.4 Å) with MIL-47-\( \text{V}^{(\text{IV})} \) than \( \text{C}_2\text{H}_4 \) (2.7 Å).

For the MFM-300 family, the MFM-300-\( \text{V}^{(\text{III})} \) [Figure 31(a)] binds the \( \text{C}_2\text{H}_2 \) in a similar way as the MIL-47-\( \text{V}^{(\text{III})} \) does, i.e., -OH interacting with the \( \pi \) electrons in the carbon-carbon triple bond. However, the distances between the hydrogen atom and the carbon atoms are about 2.9 Å, which is close to the sum of the vdW radii for hydrogen and carbon atoms and hence at the limit of the interaction range.
Figure 31: The most stable binding conformation of C$_2$H$_2$ at binding site 1 in the four MOF structures: (a) MFM-300-V$^{(III)}$; (b) MFM-300-V$^{(IV)}$; (c) MIL-47-V$^{(III)}$; and (d) MIL-47-V$^{(IV)}$. Only one molecule and the closest atoms near the binding site are shown to highlight the local binding environment.

Our result is consistent with Ref. [201], where this distance was determined to be about 3.0 Å based on NPD results. The binding distance is closer than that of C$_2$H$_4$@MFM-300-V$^{(III)}$ [Figure 28(a)], likely due to the smaller steric hindrance of the linear C$_2$H$_2$ molecule. Besides the attractive interaction between C$_2$H$_2$ and the bridging -OH group, the $\Delta\rho$ plot in Figure 32(a) shows additional contributions to the binding energy from the interactions between C$_2$H$_2$ and the linker.

Comparing with the case of C$_2$H$_4$@MIL-47-V$^{(III)}$ [Figure 30(a)], one can see small charge accumulation between the -OH and the $\pi$ electrons in the C$_2$H$_2$, consistent with the fact that C$_2$H$_2$ binds
closer to the MOF than C₂H₄. Moreover, this attractive interaction between the \( \pi \) electrons in the C₂H₂ and the bridging -OH group makes the binding energy at site 1 (44.1 kJ/mol) larger than that at site 2 (40.5 kJ/mol).

For MFM-300-V(IV), our relaxation shows that the most stable structure is a “side-on” conformation [Figure 31(b)] with a very long (4.7 Å) distance between the bridging -O atom and the carbon-carbon \( \pi \) bond. This is consistent with the NPD results reported in Ref. [201], where this distance is determined to be greater than 4.83 Å. However, we do not expect such a long distance to give rise to any interaction between the C₂H₂ and the bridging -O atom (let alone the fact that this interaction, if at all possible, must be repulsive because both species are electronegative). To understand the nature of the binding mechanism between C₂H₂ and the MOF, we analyze the \( \Delta \rho \) plot in Figure 32(b), which shows that the interaction between C₂H₂ and the cluster around the vanadium atoms is negligible. Rather, the contribution to the binding energy is mostly from the interaction between C₂H₂ and the linker, even when C₂H₂ is located at site 1. It explains why the binding energy at site 1 (40.6 kJ/mol) is comparable to that at site 2 (41.4 kJ/mol). We note in passing that we have computationally explored another “head-on” conformation (not shown) similar to that of C₂H₂@MIL-47-V(IV) [Figure 31(d)]. However, that conformation leads to a much lower binding energy (36.4 kJ/mol) than Figure 31(b) (40.6 kJ/mol), likely due to the lack of attractive interactions between the linker and the C₂H₂.

4.5 **SIGNIFICANT FINDINGS**

Overall, the bridging -OH group in MIL-47-V(III) leads to a strong binding preference compared to the site 2 of the same MOF and the site 1 of MIL-47-V(IV). Similarly, the bridging -O group in MIL-47-V(IV) leads to a weak binding preference compared to the site 2 of the same
Figure 32: The charge density difference upon binding, $\Delta \rho$, for $\text{C}_2\text{H}_2$ at (a) site 1 of MFM-300-$\text{V}^{\text{III}}$ and (b) site 1 of MFM-300-$\text{V}^{\text{IV}}$. Blue (yellow) color indicates electron charge accumulation (depletion) upon binding. The same isosurface value is used for both panels.

MOF. However, such preferences are much weaker in the MFM-300 family. There is only a slight preference in binding with site 1 compared to site 2 in MFM-300-$\text{V}^{\text{III}}$ due to the weak interaction between the bridging -OH and the $\pi$ electrons in $\text{C}_2\text{H}_2$. From a binding energy perspective, there is not much selectivity between site 1 and site 2 in MFM-300-$\text{V}^{\text{IV}}$. We again attribute the difference between MFM-300 and MIL-47 to the local steric effects near the vanadium atoms. Based on our findings, we predict that MIL-47-$\text{V}^{\text{III}}$ and MIL-47-$\text{V}^{\text{IV}}$ could also be used for hydrocarbon separation, similar to the MFM-300 family. Furthermore, comparing the $\text{V}^{\text{III}}$ and $\text{V}^{\text{IV}}$ MOF in the MIL-47 family, their difference in binding energies with unsaturated hydrocarbons is larger than those in the MFM-300 family. Moreover, the two unsaturated hydrocarbons, $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$, give rise to larger binding energies with the $\text{V}^{\text{III}}$ MOF than $\text{C}_2\text{H}_6$, in contrast to the MFM-300 family. The larger binding energy is due to the strong binding preference between $\pi$ electrons in the hydrocarbon and the bridging -OH in the MIL-47-$\text{V}^{\text{III}}$. Such results indicate that the difference in IAST selectivities between the $\text{V}^{\text{III}}$ and $\text{V}^{\text{IV}}$ MOFs in the MIL-47 family might be greater than what has been experimentally observed for the MFM-300 family in Ref. [201].
and the actual values of the selectivities might be larger than the corresponding MFM-300 values, too. We emphasize again that these differences stem from the structural difference between the MIL-47 and MFM-300, where the former has less steric hindrance near the bridging -OH group or -O atom such that the binding distance is shorter than that in the MFM-300 and the binding is more directional.
CHAPTER 5  CONCLUSIONS

The fundamental mechanistic understanding of the microscopic behavior of next generation materials is crucial in achieving a desired functionality. In this research I have evaluated three materials of interest: antiferroelectric materials, 2D hybrid organic-inorganic perovskites and metal organic frameworks. These materials have applications in energy storage technologies, light emitting technologies, and fuel energy storage. Therefore, an extensive study on the connections between their microscopic behavior and macroscopic properties was necessary. In this work I have applied both theoretical first principles calculations and experimental vibrational spectroscopy techniques.

5.1 CHAPTER 1

In Chapter 1 I began with a brief introduction into the importance of improving the energy efficiency and energy storage technologies in our society. I described the gap in the material science community where we have yet to identify the ideal material or a sufficient understanding of the energy-conversion mechanisms. I described the prototypical Ragone plot which describes the roles of energy storage systems we use in society, and how we can begin to develop materials with high power and energy density. The first step in bridging this gap is first understanding how the material influences its structure and thus the properties and performance. The three materials of interest in this work include: antiferroelectrics, hybrid perovskites and metal organic frameworks. Each material we study has their unique structure, but understanding how changes to their structure contribute to its physical observables (structure-property relationships) in energy related applications is the bridge between my projects.
5.2 CHAPTER 2

In Chapter 2 I explicitly described my work relating to the antiferroelectric material of interest, 2-trifluormethylbenzimidazole (TFMBI). Here we have considered the fundamental physical mechanism explaining the temperature-dependent shifts of peaks in the polarized Raman spectra of single crystals of the hydrogen-bonded material TFMBI in a structure previously shown to possess antiferroelectric order. Our temperature dependent measurements have led us to report a new structure of TFMBI at low temperatures in which the unit cell doubles along the \( c \)-axis and distorts slightly. We first tested whether the vibrational Stark effect could account for the vibrational frequency shifts we observed. However, we did not find a consistent shift across the different regions of our Raman spectra.

We then considered structural anharmonicity. By modeling the positions of three peaks assigned to the aromatic ring distortion vibrations of TFMBI molecules by DFT calculations, we find the quartic anharmonic contribution to the interatomic potential energy of the crystal can account for the observed shifts appropriately. Using a fitting analysis to a model function describing the shift expected from this anharmonic interaction energy, we find our fits depend sensitively on the value of the purely harmonic vibrational frequency. Specifically, we find the fits improve as we bring the harmonic frequency closer to that of the peak positions found experimentally. This fact both substantiates our proposal that a temperature-independent quartic anharmonicity accounts for the peak shifts and indicates the DFT calculations we use to model the harmonic vibrational frequency overestimate these values significantly. Moreover, our analysis indicates the strength of the anharmonic coupling causing the shift in the peak position of the three examined modes does not change as a function of the hydrogen-bonding structure of the monoclinic phase in which we
measure the Raman spectra. Figure 33 summarizes these results.

Figure 33: 2-trifluormethylbenzimidazole modeled unit cell and temperature dependent Raman shift.

In summary, the frequencies of intramolecular vibrations have gained attention as probes of highly localized electrostatic structures in biological and synthetic catalytic applications. In those cases, one uses the vibrational Stark effect to assess the strengths of nano- and microscopic electric fields capable of shifting vibrational levels linearly. While such an approach could provide critical information about the microscopic electrostatic environment of hydrogen-bonded antiferroelectric materials composed of molecules central to the energy storage capabilities, our results indicate researchers must take great care in the analysis of vibrational peak shifts in response to external stimuli, especially temperature. Since the vibrational Stark effect necessitates a constant structural anharmonicity, one must systematically and thoroughly eliminate the possibility that any and all peak shifts stem from anharmonic contributions due to changes in hydrogen-bonding structure and interactions. Only such an elimination will enable one to decipher the microscopic electrostatic drivers of macroscopic properties in this interesting class of materials.
5.3 CHAPTER 3

In Chapter 3 I discussed the results from the work regarding the 2D hybrid organic-inorganic perovskites. This involved first understanding the nature of the coupling between the organic cation and inorganic octahedral framework. To gain insight into such light emitting applications we must first fundamentally understand the structure of this material. We propose the NH$_3^+$ ammonium group is the driving force behind the electrostatic interaction of the organic cation and octahedral framework. In this chapter, using a combination of Raman spectroscopy in the backscattering geometry and first-principles calculations, we characterized the Raman spectra of four similarly structured two-dimensional hybrid organic-inorganic perovskites, hexyl-ammonium lead iodide, hexyl-ammonium lead bromide, butyl-ammonium lead iodide and benzyl-ammonium lead iodide. We focused on the 1400-1600 cm$^{-1}$ range where the ammonium bending modes dominate the Raman intensity. We first obtained normal-mode eigenvectors from DFPT using LDA functional and then performed frozen-phonon calculations using the vdw-DF-cx functional for a series of geometries with atoms displaced along the DFPT normal-mode eigenvectors. We found this strategy leads to a quantitative agreement between experiment and computation, which helped us in unambiguously assigning experimental Raman peaks as normal modes of the crystal. We discussed the relationship between the ammonium bending modes in the periodic crystal and in the isolated organic cation and found that a PbX$_3^-$ (X=Br or I) fragment placed next to the organic cation could successfully explain the crystal effect on the ammonium bending modes. We conclude that these ammonium bending modes could serve as a useful experimental probe to the microscopic structure of the lead halogen octahedra that form the lattice framework of the 2D HOIP crystal. Figure 34 shows the relationship we find between the crystal structure and isolated organic cation with a PbI$_3^-$
Once we gained a good foundation on the structure and the coupling between the layers of our 2D HOIP materials, we then approached the mechanism behind the photoluminescence features we observe. The understanding of the mechanism driving these PL features will allow one to synthesis these perovskites for desired functionality in light emitting applications. Literature shows there are two typical studied driving forces, either self-trapped excitons and/or defects. I explored using first principles calculations the role defects play in the PL features we observe. Using the insight we gained from the coupling of the layers, I modeled defects associated with the ammonium group and the nearby lead and iodine atoms. The first defective structure I modeled was the removal of one iodine and the nearest hydrogen atom of the organic cation. I performed band structure calculations, molecular orbital calculations, and projected density of states calculations. I used the PBE functional as well as the HSE functional. We observed a non-dispersive band in our
band structure calculations. The project density of states calculation also agreed with the band structure as there was charge buildup in the bandgap. This consisted of mostly the nitrogen p orbitals. We find the combination I\(^-\) and H\(^+\) vacancies produce a localized electronic state in an energetic vicinity consistent with our experimental results. We also explored just an iodine vacancy. However, we did not observe a predicted mid-gap nor charge buildup in the bandgap of our predicted projected density of states calculation. Figure 35 summarizes our results.

![Figure 35: PBE predicted band structure of hexyl-ammonium lead iodide. Pristine structure in blue and defective (removal of I and H) structure in red. Molecular orbital plot of flat nondispersive band indicating charge is localized near defect site.](image)

### 5.4 CHAPTER 4

In chapter 4 I describe my computational work on the metal-organic frameworks, specifically MIL-47-V(III), MIL-47-V(IV). MOFs are important in several applications; however, our focus is on gas storage and gas adsorption for the MIL-47 family of MOFs. Our goal is to understand the binding mechanism of hydrocarbons in MIL-47. We focused on MIL-47 as its porous structure is without an open metal site. We studied the binding of four small hydrocarbons CH\(_4\), C\(_2\)H\(_6\), C\(_2\)H\(_4\), and C\(_2\)H\(_2\) to the pores of these vanadium-based MOFs. We consider two structures V(III) and
V(IV) for the MIL-47 MOFs. We consider two binding sites as well. One binding site is near the bridging -OH or -O group that connects two neighboring vanadium atoms and the other site located close to the linker. We carried out first-principles density functional calculations using the vdw-DF-cx functional. We demonstrated a preference in binding with the unsaturated hydrocarbons at the site 1 of the V(III) based MIL-47 MOF. We conclude that the -OH or -O group acts as a pseudo-open metal site that provides the necessary binding preference and selectivity. Our results explain existing hydrocarbon separation experiments from a binding perspective. The structure-property relationships we uncovered could provide insight into the future design of similar porous materials. Figure 36 summarizes the MIL-47 vanadium-based MOF results.

![Figure 36](image)

**Figure 36:** Left panel: MIL-47-V(III) binding to C2H2 site 1, with a binding energy of 45.25 kJ/mol. Right panel: The predicted charge density plot of C2H2 binding to site 1 of MIL-47-V(III). (Yellow positive, blue/red accumulation of density upon binding).

### 5.5 SUMMARY AND FUTURE

This work developed fundamental insights into the electronic behaviors of three next-generation materials: 2-trifluormethylbenzimidazole, 2D lead iodide perovskites, and vanadium based MOFs. We focused on bridging the gap between experiment and theory to provide our in-
sights. We began to understand how the material influences its structure and thus its properties; hence the structure-property relationships. We provided insights into the mechanisms driving their energy related applications. Future efforts such as the consideration of structural anharmonicity in vibrational peak shifts in antiferroelectric materials and how defects influence light emission in perovskites are still needed to meet the energy demands we face. Ultimately, this work contributes towards the achievement of desired functionality in energy related applications of next-generation materials.
APPENDIX A

Figure 37 compares the measured powder x-ray pattern diffracted from TFMBI samples formed using the approach described in the Methods section of the main text to the pattern expected from a structural model found by applying Le Bail’s method[65] using the General Structure Analysis System (GSAS-I)[66]. We refined the following parameters: (1) scale factor; (2) background, which was modeled using a shifted Chebyshev polynomial function; (3) peak shape, modeled using a modified Thompson-Cox-Hasting pseudo-Voigt function; (4) lattice constants; and (5); an isotropic displacement parameter for all atoms. Difference curves and Rwp (weighted profile) residuals were employed to assess the quality of the refined structural models. The agreement between the measured and modeled patterns suggests we do not form crystalline phases besides the $P2_1/c$ phase of TFMBI known to be anti-ferroelectric from the work of Horiuchi et al.[41].

Solution Phase Raman Spectrum of TFMBI in DMF  As we find in Figure 38, a broad peak appears near 3480 cm$^{-1}$ in a 50 mM concentration solution of TFMBI in DMF. Based on DFT calculations of the vibrational spectrum of individual gas phase TFMBI molecules we assign this peak as corresponding to the molecule’s N-H stretching vibration. In contrast to this solution phase spectrum, the vibrational Raman spectrum of crystalline TFMBI shows the N-H stretching vibration red shifts to below 3100 cm$^{-1}$. This difference between the solution and solid phase spectrum indicates hydrogen bonding increases substantially when forming crystalline TFMBI relative to the solution.

Maradudin and Fein show the quartic contribution to Eq. 5.1 can induce a first order perturbative shift of the vibrational frequency when a different vibrational mode interacts twice, first creating a quantum of the perturbing vibration and then annihilating it[57]. This virtual phononic
interaction changes the energy of the perturbed vibrational mode and causes shifts in spectra measured via light absorption and scattering. Furthermore, this first order correction is unweighted by the energy difference between the unperturbed vibrational wavefunction and its perturbing counterpart. Based on these considerations, we only treat terms in the quartic contribution to the expansion of the interatomic potential energy of the form,

\[
\frac{1}{4!} \left( \frac{\partial^4 U}{\partial Q_1^2 Q_2^2} \right)_0 Q_1^2 Q_2^2 = g_{12} \left( \hat{a}_1 + \hat{a}^\dagger_1 \right)^2 \left( \hat{a}_2 + \hat{a}^\dagger_2 \right)^2 ,
\]  

(5.1)
Figure 38: Comparison of the Raman spectrum of a 50 mM solution of TFMBI in DMF in the region of the N-H stretch of the solute to that of neat DMF.

where we define,

\[ g_{12} = \frac{1}{4!} \left( \frac{\partial^4 U}{\partial Q_1^2 Q_2^2} \right)_0 \frac{\hbar^2}{4 \mu_1 \omega_1 \mu_2 \omega_2}, \]  

(5.2)

in order to write the quartic anharmonic term using the creation and annihilation operators, \( \hat{a}_i \) and \( \hat{a}_i^\dagger \), corresponding to each vibrational mode. The terms \( \mu_1 \) (\( \mu_2 \)) and \( \omega_1 \) (\( \omega_2 \)) in Eq. 3 correspond to the reduced mass and frequency of the 1st (2nd) vibrational mode of TFMBI, which interest us in this study. One can rationalize \( g_{12} \) as changes in the strengths of chemical bonds involved in the \( Q_1 \) mode when an excitation in the \( Q_2 \) mode is present.

When we add the interaction term of Eq. 5.2, the total vibrational Hamiltonian in quantized
form becomes,

$$\hat{H}_{\text{tot}} = \sum_{i=1}^{2} \hbar \omega_i \hat{a}_i^\dagger \hat{a}_i + g_{12} \left( \hat{a}_1 + \hat{a}_1^\dagger \right)^2 \left( \hat{a}_2 + \hat{a}_2^\dagger \right)^2 = \hat{H}_0 + \hat{H}', \quad (5.3)$$

where we have offset the vibrational energies by amounts stemming from their zero point motions, i.e. $\hbar \omega_i/2$. To treat the effects of $\hat{H}'$, we presume the total wavefunction can be expanded as a product of the wavefunctions corresponding to the individual harmonic normal modes of the material, which we write as,

$$|\Psi\rangle_{\text{vib}} = \prod_i |n_i\rangle_i, \quad (5.4)$$

where $n_i$ indicates the average occupation number of the $i$th mode at a temperature $T$ dictated by Bose-Einstein statistics. Using standard time independent perturbation theory with these wavefunctions, we find the first order correction to the vibrational energy due to the quartic anharmonic term becomes,

$$E_{n_1}^{(1)} =_{\text{vib}} \langle \Psi | \hat{H}' | \Psi \rangle_{\text{vib}} = 2 \langle n_2 | n_1 | g_{12} \left( \hat{a}_1 + \hat{a}_1^\dagger \right)^2 \left( \hat{a}_2 + \hat{a}_2^\dagger \right)^2 |n_1\rangle_1 |n_2\rangle_2$$

$$\quad \quad \quad = g_{12} (2n_1 + 1)(2n_2 + 1), \quad (5.5)$$

where $n_1$ and $n_2$ are the average occupations of the 1st and 2nd modes at a temperature $T$.

We note an important facet of the fundamental physical interpretation of Eq. 5.5. This equation shows that despite the fact that the ground state of the 1st mode may possess an average occupation of zero, i.e. $n_1 = 0$, the interaction with virtual vibrations of the 2nd mode can still cause a first
Table 3: Comparisons of the interaction energies, $g_{12}$, and effective coupled mode frequencies, $\omega_c$, for the quartic anharmonic contribution to the vibrational mode frequencies of the ring vibrations of TFMBI. These results are found by fitting temperature dependent vibrational Raman peak shifts to Eq. 2.2 for different values of the harmonic vibrational frequency, $\omega(0)/2\pi c$ in each $P2_1/c$ structure of the material. An asterisk indicates harmonic frequencies found from DFT calculations.

<table>
<thead>
<tr>
<th>mode</th>
<th>Structure 1 ($T \geq 198$ K)</th>
<th>Structure 2 ($T &lt; 198$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_3$</td>
<td>$\omega(0)/2\pi c$ [cm$^{-1}$]</td>
<td>$g_{12}/\hbar c$ [cm$^{-1}$]</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1274</td>
<td>5.0±0.02</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1345$^*$</td>
<td>38.8±0.1</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1414</td>
<td>6.0±0.3</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>1473$^*$</td>
<td>36.6±0.2</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>1556</td>
<td>2.1±0.18</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>1634$^*$</td>
<td>42±0.5</td>
</tr>
</tbody>
</table>

order correction to the ground state energy of this higher energy intramolecular vibration, as we expect would be necessary to cause a vibrational peak shift. Based on Eq. 5.5, we write the perturbed frequency corresponding to the fundamental vibrational transition, $\omega'$, as

$$\omega' = \frac{1}{\hbar} \left( E_1^{(0)} + E_1^{(1)} - E_0^{(0)} - E_0^{(1)} \right) = \omega^{(0)} - 2 \frac{g_{12}}{\hbar} (2n_2 + 1),$$  \hspace{1cm} (5.6) 

where $\omega^{(0)}$ is the harmonic frequency of the fundamental vibrational excitation we find from DFT calculations.
Figure 39: ACS permission to include my published work: Sydney N. Lavan, Cathleen A. Saraza, Kanwar Bhullar, Sardou Sabeyo-Yonta, Adedayo M. Sanni, and Aaron S. Rury. Structural Anharmonicity Explains Continuous Frequency Shifts of Intramolecular Ring Vibrations in a Hydrogen-Bonded Antiferroelectric Crystal. The Journal of Physical Chemistry C 2020 124 (24), 12933-12947 DOI: 10.1021/acs.jpcc.0c02294 Copyright 2020 American Chemical Society.
### Table 4: A comparison of crystallographic parameters between experiment and DFT calculations.

The experimental works reporting the crystallographic parameters of each material are cited next to the experimental values.
Table 5: All Raman active modes of (HA)$_2$PbI$_4$ between 1400 cm$^{-1}$ and 1600 cm$^{-1}$. The corresponding peak numbers in Figure 15, and the values of the six orientation-dependent contributions to the Raman intensity are shown next to each mode. All Raman intensities are in atomic units.

<table>
<thead>
<tr>
<th>Peak number in Figure 15</th>
<th>Frequency (cm$^{-1}$)</th>
<th>$A_g$</th>
<th>$B_g$</th>
</tr>
</thead>
<tbody>
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<td>$xx$</td>
<td>$yy$</td>
<td>$zz$</td>
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<td>-</td>
<td>1400.0 $A_g$</td>
<td>0.07</td>
<td>0.05</td>
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<tr>
<td>-</td>
<td>1403.8 $B_g$</td>
<td>0.07</td>
<td>0.05</td>
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<td>2.35</td>
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<td>1, 6</td>
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<td>0.09</td>
<td>7.44</td>
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<td>-</td>
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<td>7.44</td>
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<td>-</td>
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<td>12</td>
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<td>15</td>
<td>1536.4 $B_g$</td>
<td>1.50</td>
<td>3.13</td>
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Table 6: All Raman active modes of (HA)$_2$PbBr$_4$ between 1400 cm$^{-1}$ and 1600 cm$^{-1}$. The corresponding peak numbers in Figure 17 of the main text, and the values of the six orientation-dependent contributions to the Raman intensity are shown next to each mode. All Raman intensities are in atomic unit, i.e., Bohr$^4$/amu, where amu is the atomic mass unit.

<table>
<thead>
<tr>
<th>Peak number of the main text</th>
<th>Frequency (cm$^{-1}$)</th>
<th>$A_g$</th>
<th>$B_g$</th>
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<td>-</td>
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<tr>
<td>17</td>
<td>1553.8 $B_g$</td>
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Figure 40: A schematic view of the normal mode eigenvectors of all (HA)$_2$PbBr$_4$ modes that are included in Figures 17 (b)(c)(d) of the main text. The red arrows depict the direction and magnitude of the vibrational movements for each atom. The peak number in Figure 17 of the main text, frequency, and symmetry for each mode are also shown.
<table>
<thead>
<tr>
<th>Peak number in Figure 6 of the main text</th>
<th>Frequency (cm$^{-1}$)</th>
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Table 7: All Raman active modes of (BA)$_2$PbI$_4$ between 1400 cm$^{-1}$ and 1600 cm$^{-1}$. The corresponding peak numbers in Figure 18 of the main text, and the values of the six orientation-dependent contributions to the Raman intensity are shown next to each mode. All Raman intensities are in atomic units.
Figure 41: A schematic view of the normal mode eigenvectors of all (BA)$_2$PbI$_4$ modes that are included in Figures 18 (b)(c)(d) of the main text. The red arrows depict the direction and magnitude of the vibrational movements for each atom. The peak number in Figure 18 of the main text, frequency, and symmetry for each mode are also shown.
Table 8: All Raman active modes of (BNA)$_2$PbI$_4$ between 1400 cm$^{-1}$ and 1600 cm$^{-1}$. The corresponding peak numbers in Figure 19 of the main text, and the values of the six orientation-dependent contributions to the Raman intensity are shown next to each mode. All Raman intensities are in atomic units.
Figure 42: A schematic view of the normal mode eigenvectors of all (BNA)$_2$PbI$_4$ modes that are included in Figures 19 (b)(c)(d) of the main text. The red arrows depict the direction and magnitude of the vibrational movements for each atom. The peak number in Figure 19 of the main text, frequency, and symmetry for each mode are also shown.
Figure 43: One-dimensional potential energy curves along the normal-mode coordinates of (HA)$_2$PbBr$_4$, for (a) peak 15 and (b) peak 17 in Figure 17 of the main text. Solid lines represent the quadratic fitting used to calculate the phonon frequency from each functional.

Figure 44: One-dimensional potential energy curves along the normal-mode coordinates of (BA)$_2$PbI$_4$, for (a) peak 15 and (b) peak 16 in Figure 18 of the main text. Solid lines represent the quadratic fitting used to calculate the phonon frequency from each functional.

Figure 45: One-dimensional potential energy curves along the normal-mode coordinates of (BNA)$_2$PbI$_4$, for (a) peak 13 and (b) peak 16 in Figure 19 of the main text. Solid lines represent the quadratic fitting used to calculate the phonon frequency from each functional.
Figure 46: The three groups of Raman-active ammonium bending modes in the (HA)$_2$PbBr$_4$ crystal (where there are two modes in each group), compared to the corresponding modes in an isolated HA$^+$ cation and a charge-neutral system that consists of a HA$^+$ cation placed next to a PbBr$_3$ fragment. All frequencies are from LDA-based DFPT. (a) Symmetric ammonium bending. (b) Asymmetric ammonium bending. (c) Another asymmetric ammonium bending, with different atomic displacement patterns than (b).
Figure 47: The three groups of Raman-active ammonium bending modes in the (BA)$_2$PbI$_4$ crystal (where there are four modes in each group), compared to the corresponding modes in an isolated BA$^+$ cation and a charge-neutral system that consists of a BA$^+$ cation placed next to a PbI$_3^-$ fragment. All frequencies are from LDA-based DFPT. (a) Symmetric ammonium bending. (b) Asymmetric ammonium bending. (c) Another asymmetric ammonium bending, with different atomic displacement patterns than (b).
Figure 48: The three groups of Raman-active ammonium bending modes in the (BNA)$_2$PbI$_4$ crystal (where there are four modes in each group), compared to the corresponding modes in an isolated BNA$^+$ cation and a charge-neutral system that consists of a BNA$^+$ cation placed next to a PbI$_3^-$ fragment. All frequencies are from LDA-based DFPT. (a) Symmetric ammonium bending. (b) Asymmetric ammonium bending. (c) Another asymmetric ammonium bending, with different atomic displacement patterns than (b).
Figure 49: Powder diffraction of (HA)$_2$PbBr$_4$ showing the reflections from (00$l$) and other planes in the material, which are consistent with the formation of a 2D layered material. We acquired powder XRD pattern using a Bruker D8 powder diffractometer operated at 40 kV and 40 mA. We employed Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) to obtain patterns in the 3.5-65° 2θ range using a step size of 0.0122° and a step time of 1.5 s.
Figure 52: ACS permission to include my published work: Sydney N. Lavan, Adedayo M. Sanni, Aaron S. Rury, and Zhenfei Liu. Characterization of the Ammonium Bending Vibrations in Two-Dimensional Hybrid Lead-Halide Perovskites from Raman Spectroscopy and First-Principles Calculations. The Journal of Physical Chemistry C 2021 125, 1, 223-236 DOI: 10.1021/acs.jpcc.0c09621. Copyright 2021 American Chemical Society.
APPENDIX C

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Table 9: Calculated crystallographic parameters in Å. In our relaxations, we constrain the symmetry of the MFM-300 family as tetragonal, as determined experimentally [201]. We constrain the symmetry of the MIL-47 family as orthorhombic, consistent with Ref. [198].

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Table 10: The calculated binding energy per molecule in kJ/mol between each of the four MOFs and each of the four hydrocarbons. For each MOF-hydrocarbon pair, we list results for the most stable conformation at each of the two binding sites.
REFERENCES


Deping Qian, Bo Liu, Suhao Wang, Scott Himmelberger, Mathieu Linares, Mikhail Vagin, Christian Müller, Zaifei Ma, Simone Fabiano, Magnus Berggren, Alberto Salleo, Olle In-


[87] Stephen D. Fried, Sayan Bagchi, and Steven G. Boxer. Measuring electrostatic fields in both hydrogen-bonding and non-hydrogen-bonding environments using carbonyl vibra-


Seham K. Abdel-Aal, Gudrun Kocher-Oberlehner, Andrei Ionov, and R. N. Mozhchil. Effect of organic chain length on structure, electronic composition, lattice potential energy, and


[125] P Giannozzi, O Andreussi, T Brumme, O Bunau, M Buongiorno Nardelli, M Calandra, R Car, C Cavazzoni, D Ceresoli, M Cococcioni, N Colonna, I Carnimeo, A Dal Corso,


Ülkü Kökçam-Demir, Anna Goldman, Leili Esrafili, Maniya Gharib, Ali Morsali, Oliver Weingart, and Christoph Janiak. Coordinatively unsaturated metal sites (open metal sites)


[192] Cristina P. Krap, Ruth Newby, Amarajothi Dhakshinamoorthy, Hermenegildo García, Izabela Cebula, Timothy L. Easun, Mathew Savage, Jennifer E. Eyley, Shan Gao, Alexan-


[196] Xinran Zhang, Ivan Da Silva, Rodrigo Fazzi, Alena M. Sheveleva, Xue Han, Ben F. Spencer, Sergey A. Sapchenko, Floriana Tuna, Eric J.L. McInnes, Ming Li, Sihai Yang, and Martin Schroder. Iodine Adsorption in a Redox-Active Metal-Organic Framework: Electrical


ABSTRACT

THE DEVELOPMENT OF FUNDAMENTAL INSIGHTS INTO THE ELECTRONIC BEHAVIORS OF NEXT-GENERATION MATERIALS

by

SYDNEY NICOLE LAVAN

May 2022

Advisors: Dr. Aaron S. Rury and Dr. Zhenfei Liu
Major: Chemistry (Physical)
Degree: Doctor of Philosophy

We develop the fundamental mechanistic understanding of the microscopic behavior of three next generation materials: antiferroelectrics, hybrid perovskites and metal organic frameworks. These materials have the potential to be used in energy and light related applications which could provide a solution for the energy efficiency challenges we face in today's society. Ideally we need to begin to bridge the gap of developing candidate materials that possess high power density and high energy density. The first step in bridging this gap is understanding how the material influences its structure and thus the properties and performance. We leverage vibrational spectroscopy and first principles calculations to provide the fundamental insight into the electronic behaviors of these three materials. The antiferroelectric materials due to their dipole arrangements leads to a higher energy storage density than ferroelectric materials. We studied the anharmonic behaviors of vibrations in 2-trifluormethylbenzimidazole (TFMBI), the antiferroelectric material of interest, using temperature-dependent Raman Spectroscopy. We find the quartic anharmonic contribution to the interatomic potential energy can account for the observed vibrational peak shifts. In addition, we find our anharmonic model fits improve as we manually adjust the harmonic frequency.
The perovskites are a layered 2D material consisting of organic and inorganic layers. We first determined the nature of the coupling between the layers and found the ammonium group is driving the electrostatics between the layers. We then examined the electronic structure of defective hexyl-ammonium lead iodide, the perovskite of interest, to understand how to control the light spectra these materials emit. We find the combination of iodine and hydrogen vacancies produce a localized electronic state in an energetic vicinity consistent with our experimental results. Metal organic frameworks are important in several applications including gas adsorption. We study two vanadium based MOFs, MIL-47 and MFM-300 with different organic linkers. We explored the binding mechanism of light hydrocarbons in the pores of our materials, focusing on the role the -OH/-O functional group plays. We conclude that the -OH or -O group acts as a pseudo-open metal site that provides the necessary binding preference and selectivity. The structure-property relationships we uncovered in these next-generation materials provides insight into the future design for desired functionality.
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Publications


