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**Ab Initio Methylammonium Orientation and Monolayer Effects in Hybrid Perovskite Solar Cells**

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AB INITIO METHYLAMMONIUM ORIENTATION AND MONOLAYER EFFECTS IN HYBRID PEROVSKITE SOLAR CELLS

A Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

by

JACOB M. ARTZ
B. S., Wright State University, 2019

2021
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Jacob M Artz ENTITLED Ab Initio Methylammonium Orientation and Monolayer Effects in Hybrid Perovskite Solar Cells BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Materials Science and Engineering.

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Methylammonium lead triiodide (MAPbI₃) has garnered attention due to their high solar cell efficiencies and low cost to manufacture, but commercialization is not yet possible owing to poor environmental stability. Thus, researchers seek ways which optimize the performance of the MAPbI₃ solar cell by modifying the architecture and through interfacial engineering of the charge transport layers. Difficulties in understanding these devices arise from ion migration, charge separation and recombination, and metastable, thermally active precessions of the methylammonium (MA) moiety in the lead iodide framework. In this work, focus is given to the perovskite and an adsorbed monolayer, 2,3,4,5,6-pentafluorothiophenol (C₆F₅SH), which has demonstrated to increase environmental stability and solar cell efficiency when placed at the perovskite/HTM interface. Utilizing a first principles approach, the interface of MAPbI₃ and C₆F₅SH is explored using various metastable methylammonium orientations to understand the relative stability, electronic properties, bandgap, and infer impact on solar cell performance.
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Relaxed PbI terminated slabs. † indicates the most stable configuration.

Relaxed MAI terminated slabs. † indicates the most stable configuration.
Three dimensional charge density plots. Isosurfaces are drawn in white, orange, red, and purple, at 0.2, 0.3, 0.4, 0.5 e/bohr$^3$ respectively.  

Three dimensional charge density plots. Isosurfaces are drawn in cyan, green, grey, yellow, orange, red, and purple, at 0.0005, 0.001, 0.005, 0.2, 0.3, 0.4, 0.5 e/bohr$^3$ respectively.

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Monolayer-modified R-II-M+m
a) Initial positions
b) Magnified view highlighting the difference in positions where the initial positions are greyed out, and the final positions are colorized.

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a) Initial positions
b) Magnified view highlighting the difference in positions where the initial positions are greyed out, and the final positions are colorized.

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a) in standard crystallographic orientation
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Charge density plots for S-M+m magnified at the interface drawn at 0.00075 eV/Bohr$^3$ isosurface values
a) in standard crystallographic orientation
b) magnified at the interface to better show charge redistribution.
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Total density of states magnified near the Fermi Energy for the pristine slabs **R-II-M** and **S-M**, and surface modified **R-II-M+m** and **S-M+m**. Each of these have been fermi shifted such that \( E(0)=E_{\text{Fermi}} \).

Projected density of states separated by elemental contribution for:
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- (top right) pristine **R-II-M**,
- (bottom left) **S-M+m**,
- (bottom right) pristine **S-M**

\( lm \)-decomposed projected density of states for:
- (top left) **R-II-M+m**,
- (top right) pristine **R-II-M**,
- (bottom left) **S-M+m**,
- (bottom right) pristine **S-M**

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List of Acronyms

ADP—Atomic Displacement Parameter
AM—Air Mass
BZ—Brillouin Zone
C₆F₅SH—2,3,4,5,6-pentafluorothiophenol
CBM—Conduction Band Minimum
FA—Formamidinium
FF—Fill Factor
FFT—Fast Fourier Transform
GGA—Generalized Gradient Approximation
HOMO—Highest Occupied Molecular Orbital
HTM—Hole Transport Material
IBZ—Irreducible Brillouin Zone
LDA—Local Density Approximation
LUMO—Lowest Unoccupied Molecular Orbital
MA—Methylammonium
MAPbI₃—Methylammonium Lead Triiodide
MD—Molecular Dynamics
ND—Neutron Diffraction
NMR—Nuclear Magnetic Resonance
PAW—Projector Augmented Method
PCE—Power Conversion Efficiency
PND—Powder Neutron Diffraction
PSC—Perovskite Solar Cell
PTAA—poly-[bis(4-phenyl)(2,3,6-trimethylphenyl)amine]
PV—Photovoltaic
SAM—Self Assembled Monolayer
SC—Solar Cell
SCF—Self Consistent Field
SCND—Single Crystal Neutron Diffraction
Spiro-OMeTAD—2,2’,7,7’-tetrakis(N,N-p-dimethoxyphenylamino)-9,9’-spirobifluorene
SQ—Shockley-Quessier
VBM—Valence Band Maximum
VESTA—Visualization for Electronic and Structural Analysis
XRD—X-Ray Diffraction
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1 Introduction

Current projections by the U.S. Energy Information Administration indicate that the global energy consumption is set to increase by 50% by the year 2050, thus, renewables and other green technologies must be developed and implemented to sustain these demands [1]. Of these green technologies, solar cells (SCs) or photovoltaics (PVs) have held a notable role in energy generation, and continue to pave the way for renewables due to the 885 million terawatt hours of solar energy that reaches the earth’s surface annually [51]. To harness this energy, there have been three main classes or generations of solar cells that are continually being developed: first generation silicon cells, second generation thin-film technologies, and third generation emerging PVs. In this work, focus is drawn to methylammonium lead(II) triiodide (CH$_3$NH$_3$PbI$_3$, MAPbI$_3$) which belongs to the third generation of solar cells.

Perovskite solar cells (PSCs) have heralded great attention due to their rapid rise in solar cell performance with the pioneering work of Kojima et al. [25] in 2009 reporting a power conversion efficiency (PCE) of 3.8%, to results now exceeding 25% [19] and rivaling silicon cells. Moreover, their relative ease of production via solution-processing and thin film technology could allow for easily manufactured, inexpensive, flexible photovoltaics. Generically, PSCs have the chemical formula ABX$_3$, wherein the A-site cation rests betwixt the BX$_6$ as shown in Fig. 1 below. For this class of materials, the A-site cation is typically a small cation, such as methylammonium (MA$^+$, chemical formula CH$_3$NH$_3^+$), formamidinium (FA$^+$, chemical formula CH(NH$_3$)$_2^+$), Rb$^+$ or Cs$^+$, the B-site cation is typically lead (Pb) or tin (Sn), and X is a halide (F$^-$, Cl$^-$, Br$^-$, I$^-$).
Akin to other perovskites, MAPbI\(_3\), undergoes phase transitions which involve movement of the BX\(_6\) octahedra and complex interplay with the A site cation. These are characterized by the sharing of corners of the PbI\(_6\) octahedra accompanied by tilting of these octahedra as shown in Fig. 2. Various experimental methods indicate that MAPbI\(_3\) exists in three main stable phases: orthorhombic, tetragonal and cubic. The low temperature orthorhombic phase is stable up to 165 K and belongs to the \textit{Pnma} space group \([61]\) and in this phase the C-N axis of MAs is locked in an anti-aligned configuration (i.e. head to tail), such that only rotations about the methyl and amine rotors are allowed. Upon heating, the \textit{I}\(_4\)/\textit{mcm} tetragonal phase develops via greater degree of freedom of MA ions and counterrotation of the PbI\(_6\) octahedra from

![Phase Diagram](image)

**Figure 1:** Structure of the perovskite crystal, adopted from \([48]\). For MAPbI\(_3\), this would represent its high symmetry cubic phase (>330 K) \([21]\).

**Figure 2:** Demonstration of phases and Glazer tilt patterns adopted by MAPbI\(_3\) at various temperatures, adopted from \([62]\).
the octahedral tilt pattern $a^+b^-b^-$ from the orthorhombic phase to the tetragonal $d^0d^0c^-$ Glazer tilt pattern [8] [13]. More focus is brought to the tetragonal within the “Literature Review” chapter, as it is the phase of interest for this study. Further heating increases induces the $Pm\bar{3}m$ cubic phase, wherein reorientation of the MA becomes more chaotic, and the octahedra align ($d^0d^0d^0$). The relatively large spaces for the A site to occupy in the APbI$_3$ structure allows for ease of modifications, and great interest in structure-property relationships.

These materials are inexpensively made via solution processed-thin-film methods, largely accepting of defects, and the chemistry of the PSC can be modified to cause shifts in the band gap of the material. This becomes an area of interest when considering the Shockley-Queisser limit, the maximum PCE attainable for a given single p-n junction for a given band gap, and construction on multi-junction or tandem cells [21]. While these properties are compelling, there are serious longterm issues due to degradation and loss of PCE in ambient environment as these cells are vehemently sensitive to humidity, and the inclusion of lead may pose future environmental concerns. Therefore, research over the past fifteen years has been directed towards: elucidating the driving factors for environmental instability [16], investigating various synthesis routes for greater stability [30], understanding the dynamics of charge carriers including ion diffusion [55], modification of transport layers for ideal charge separation [46], reduction of dimensionality and the realm of 2-D perovskites [45], and tailoring lead-free perovskites [48] among many others. In this context, there are three main objectives in this work: 1) Is it possible to replicate the experimental behavior of the multiple adopted configurations for MA ions within bulk MAPbI$_3$ using DFT and 2) Does the orientation of MA$^+$ ions impact the adsorption configuration of a thiol substituted monolayer and 3) how may device performance be impacted by either MA orientation and monolayer adsorption?
2 Literature Review

In order to assess the landscape of these materials, a comprehensive literature review was initially performed. The first assessment required understanding the ergodic nature of the methylammonium ion in these devices, and review what experimental evidence was present. From this, one then can ascribe how the motion of the MA$^+$ may relate to solar cell performance and what the tunable parameters for this system may be. When reviewing the endeavors to modulate and enhance solar cell performance, thiol derivatives and other Self Assembled Monolayer (SAM) systems, were employed by various groups [10] [2] [39] and even considered within our group previously [5].

2.1 A-Site Disorder Within the Perovskite Lattice

There have been a plethora of new techniques to characterize perovskites. From a crystallographic standpoint, two main techniques are used to determine the positions of the atoms: X-Ray Diffraction (XRD) and Neutron Diffraction (ND). These techniques, although functioning through similar principles, can provide higher specificity for the different species in the tetragonal MAPbI$_3$ crystal. When using XRD, the high energy photon interacts most strongly with the electron density, meaning that atoms with little electron density (such as hydrogen) are often lost in the noise. For atoms in MAPbI$_3$, this means that lead and iodine will dominate the scattering in XRD experiments and provide high sensitivity for their respective positions. As a consequence, the scattering intensity for carbon and nitrogen will be nearly indistinguishable from each other and hydrogen may be lost within the noise. In comparison,
ND offers a unique ability to observe the nature of hydrogen and other light atoms in a system [42]. Hydrogen in particular is a unique case, as deuterium and hydrogen have neutron scattering lengths of opposite signs, $6.671 \text{ fm}$ and $-3.7406 \text{ fm}$ respectively [49]. While this could potentially show isotopic preferences in a system, more-often the negative scattering length of hydrogen is used in Fourier analysis of Fourier mappings of neutron density, where the hydrogen will cause a ‘hole’ in the neutron Fourier map. This negative region can be used to quite confidently determine the positions of hydrogen with greater accuracy than possible with XRD.

Additional advantages with ND with respect to XRD is the ability for neutrons to distinguish between atoms of similar atomic number, especially when occupying the same crystallographic site. This is the case for MAPbI as C ($Z = 6$) and N ($Z = 7$) occupy the same Wyckoff position [44], however, the neutron scattering lengths are $6.6511 \text{ fm}$ and $9.37 \text{ fm}$ for the most abundant isotopes of $^{12}\text{C}$ and $^{14}\text{N}$ respectively [49]. Thus, a similar identification, as done for H, can be performed to elucidate specifically the presence of C or N.

A complete picture is garnered when the two experiments, XRD and ND, are combined. Under the same temperature conditions, the anisotropic atomic displacement parameters (ADPs) can be collected for H, C, and N using ND and properly scaled with the ADPs acquired for Pb and I from XRD. It is worth noting that Piccoli et al. suggests that Powder Neutron Diffraction (PND) is more susceptible to impurities and inner-filtering effects for strongly interacting elements (i.e. large cross-section), and incoherent scattering from deuterated samples may decrease the interpretability the experimental results, rather than provide clarity [42].

### 2.1.1 Anisotropic Displacement Parameters

In mentioning the experimental methods for determining crystal structures, it is necessary to understand the configurational uncertainties that may be present within
the system. With reference to this, measurements of the mean-squared displacement for a given atom is given by an atomic displacement parameter or matrix. This provides an idea of some of the configurational uncertainty that is present for a given system due to motion of atoms, such as thermal motion, or other static displacive disorder. Since diffraction techniques deal with the interaction of an X-ray/neutron with the electronic/neutron density, the measurement that is taken is from the reflection and hence the diffraction pattern [56]. The diffraction data then can be used to determine the crystallographic reciprocal lattice. Furthermore, scattering or form factor for a reflection can be related to the ADPs and through some mathematical manipulation, software is able to determine the mean-square displacement in the principal directions for a given atom from a reflection. More derivation on how this is implemented can be found in Trueblood et al. [56], and Grosse-Kunstleve and Adams [14].

ADPs in the perspective of perovskites are significant due to the observed motion of the cations and flexibility of the PbI$_6$ octahedra. This is best demonstrated by the refined structure as reported by Ren et al. [44] via single crystal neutron diffraction (SCND).

As shown in Fig. 3, there is seemingly indistinguishability for several positions of MA$^+$ and variance in the positions of the iodine atoms. The use of these ADPs allows for one to assess the the overlap with experimental results, which is the first step to our DFT analysis.
2.1.2 Indicators of Cation Reorientation

There have been no short supply of techniques that have been used to elucidate the dynamics of MA\(^+\). One of the first techniques to characterize the cation rotation in lead halide perovskites was performed by Wasylishen et al. in 1985, using Nuclear Magnetic Resonance (NMR) to measure spin lattice relaxation times and related rotational correlation times of deuterated samples [60]. In the tetragonal phase, they noted that long lattice relaxation times \(T_1(^2\text{H})=4.76\text{s at 303K}\) indicates rapid rotation about the C-N axis, but become restricted at lower temperatures.

Another such method is the use of quasi-elastic neutron scattering, which enables one to determine the change in momentum and energy from an incident neutron to a scattered one. One then can show that this experiment can be used to determine the activation energy for a given dynamic event (i.e. bond rotation, movement, etc.). Leguy et al. [29], performed this experiment to show that, in the temperature range of 140-370 K, \(\pi\)-flips about the C-N axis are disallowed - tumbling about the C-N axis is independent of temperature within this range and follows a 'wobbly cone' with realignment taking about 14 ps requiring 52 meV to do so. It was also demonstrated that within the time-window of 1.2 – 53 ps, no translation of the MA\(^+\) ions were observed. On the other hand, they also demonstrate that free rotation of the hydro-
gens about the methyl- and ammonium- rotor does increase with temperature with an Arrhenius activation energy of 9.9 meV.

More recently, Senocrate et al. [50], explored the motion of MA$^+$ using multinuclear solid state NMR and $^{127}$I nuclear quadropolar resonance in tandem with Molecular Dynamics (MD) simulations. A key goal of their work was to connect ion dynamics to the long carrier lifetimes in the perovskite systems. In alignment with the previous NMR work, free rotation about the C-N axis was observed, but due to the multiple element analysis, it was possible to observe a biaxial rotation of the MA$^+$ moiety. It was also noted that this biaxial rotation evolves to a nearly isotropic motion above the cubic transition temperature, which disrupts the hydrogen bonding that exists with the inorganic framework.

One of the most pivotal works was that of Stoumpos et al. [54], which still remains one of the most cited papers regarding perovskite solar cells. This work indicated the presence of disorder within the sites of the octahedra, and the resultant XRD demonstrates the relative ease of elucidating the lead and iodine framework. Unfortunately, the modes of MA$^+$ rotation were left unidentified. That is not to discredit this work though, which identified so much of the electronic properties, such as the band gap ($\sim 1.5eV$), synthetic methods, photoluminescence data, and inferences on the impact of electric field on the permanent dipoles of MA$^+$. Due to the tremendous impact this article has had, as well as it being the initial structure for many other studies, the MA$^+$ alignment from their work is one of the orientations considered within this work [54].

While there are many others that assess the reorientation of methylammonium within MAPbI$_3$, two are briefly mentioned that use ND. Weller et al. [61], assessed the evolution of the phase transitions and MA$^+$ motion using PND over the range of 100-352 K. Figure 4 shows the dramatic changes in the Bragg’s peak intensities over the aforementioned temperature range.
Figure 4: 2D NPD data over the range of 67° – 88° illustrating the phase transitions that occur at 165 and 327K within MAPbI₃. Adopted from [61].

This result clearly demonstrates the phase change over the temperature range, but their results also indicate that the orientation of the MA ions reorient and exist in a rotationally disordered state. They infer that the MA ions non-preferentially aligns toward the PbI₆ octahedral faces in the ab plane, the [100], [001], [010], and [010] directions in the tetragonal phase. At room temperature, the thermal motion increases within the ions which is sufficient to overcome the hydrogen bonding from the amine and methyl groups which also slowly moves the ion closer to the center of the A-site cavity as temperature increases. Due to the thermally dependent rapid motion of the MA cations, and the more isotropic effects on the lattice become, the PbI₆ lattice becomes less distorted at higher temperature and the $a^0a^0c^-$ tilt system gives rise to the non-tilted $a^0a^0a^0$ system [61].

To parallel these results, work done by Ren et al. [44] used SCND to examine the ordering of the tetragonal and cubic phases of MAPbI₃. Their work indicated that the amine is disordered in four positions, but due to the symmetry of the $I₄mcm$ point group, the methyl group is disordered in eight positions. Specifically, this is due to the $4b$ site having $D_{2d}$ symmetry, while MA exists in a lower symmetry group $C_{3v}$ [44]. To illustrate this, the positive nuclear density collected for MA is shown in
Fig. 5 below. This figure also depicts the opposing orientations of nearest neighbors of MA, which infers opposing dipole moments within the structure.

![Diagram of molecular structures](image)

**Figure 5**: Positive 3D difference Fourier maps from SCND for MAPbI$_3$ from [44] 
(a) Illustrating the four sites available to nitrogen and eight possible locations for carbon. 
(b) Demonstration of the necessary symmetry of the $I_4/mcm$ and visualization of a tetragonal supercell.

Due to the comprehensive set of data that was provided by Ren et al., four parallel orientations that were ascribed to the positions of the nitrogens are used in this work. Additionally due to the comments on NPD vs. SCND of Piccoli et al., adoption of the values from SCND may yield better results due to lack of incoherent scattering potentially present powder samples [42].

### 2.2 Solar Cell Performance

After asserting that cation movement is ergodic and active at room temperature, for the purpose of this work an understanding of how this ionic motion impacts the performance of solar cells is required. Moreover, it is helpful to detail the *de facto* standard metrics and operation as related to solar cells.
2.2.1 The Detailed Balance Limit

As detailed in the classic work of Shockley and Quessier, there must be a theoretical limit to the Power Conversion Efficiency, PCE or $\eta$, of single $p$-$n$ junction solar cells [52]. This result is generally referred to as the detailed balance limit. Considering the operation of such devices, the spectral irradiance can be assumed in several forms, a uniform black body emitter at approximately the temperature of the sun, 6000 K, or solar spectrums which have been meticulously outlined for uniform measurement of solar cell devices via the American Society of Testing and Materials [38]. Drawbacks to the blackbody spectrum is that it fails to account for gaseous species that interact with the photonic energy, resulting in dips in the spectral irradiance that makes it to earth. Several datasets exist for spectral irradiance, which include the AM0, a spectra which lies outside the earth’s atmosphere and most closely mirrors the black body spectrum and the AM1.5G, and AM1.5D. Of these, the most important for this discussion in the AM1.5G spectrum, as the AM1.5D is used for concentrator solar cells and the AM0 spectra is used for upper atmospheric PVs which are not considered in this work. The AM1.5G spectrum assumes an air mass of 1.5 which represents a zenith angle of $48.2^\circ$, and is tilted at $37^\circ$ to allow for collection of diffuse spectral irradiation [38]. In considering the form of the total power that is making it to the earth, the choice of solar spectrum matters as it determines the total photonic energy, and impacts uniformity of measurements. For instance, due to the integrated power density, the measure of available photonic energy, of 1000.4 $\frac{W}{m^2}$ of the AM 1.5G solar spectrum compared to the 1576.7 $\frac{W}{m^2}$ of the blackbody emitter, two similar cells may not have the same PCE. These spectrums, as well as other solar spectrums are shown in Fig. 6.

If one then considers a single bandgap semiconductor where it is assumed at photon energies greater than or equal to the bandgap, the absorbance is unity, and for all photons with energy less than the band gap the absorbance is zero. It is also
assumed that for the cell, the emission losses result from the front and rear side of the device. The initial Shockley-Quessier (SQ) limit was found for the 6000K black body emitter to be at a bandgap of 1.1 eV with a maximum theoretical efficiency of $\eta = 44\%$ [52], for the AM 1.5G solar spectrum Rühle [47] derives that the measurement is likely closer to $\eta = 33.16\%$ corresponding to a bandgap of 1.34 eV due to the absorption bands present in the solar spectrum. In the table provided by Rühle, this corresponds to a short circuit current, $J_{sc}$, of 35.03 mA cm$^{-2}$, open circuit voltage, $V_{oc}$, of 1.066V and fill factor which is $\frac{J_{mpp}V_{mpp}}{V_{oc}J_{sc}}$, $FF$, of 88.8%. To emphasize, these are values attained for single junction cells, and not concentrator or multijunction cells which have exceeded these PCE values. Greater explanation of the detailed balance limit is within the Methods section as theoretical discussion of solar cell performance can be ascribed to changes in band gap. Unfortunately, this model is insufficient when attempting to model the stacked architectures of archetypal PSCs due to complex losses in charge extraction and separation at the interfaces of the Electron Transport Material (ETM), Hole Transport Material (HTM) and within the perovskite, but are theoretically useful.
2.2.2 Typical Perovskite Solar Cell Architectures and the HTM—Perovskite Interface

Perovskite architectures are generally of the form of n-i-p, shown in Fig. 7. These are common to thin-film structures where an intrinsic layer is sandwiched within n- and p-doped regions [22]. Within this figure, the operation of the solar cell is apparent; photoexcitation occurs within the perovskite, generating an electron-hole pair. Upon successful charge separation, the respective carriers are directed towards their respective transport later and current is generated. Choice of charge transport layers are of upmost importance in high performance solar cells, as the mechanism by which charges are extracted impact nearly all device parameters [46].

Figure 7: Sandwich view of the n-i-p device architecture, and its respective energy alignment. Adopted from [46].

Typical HTM layers are relatively large, bulky aromatics such as Spiro-OMeTAD (2,2’,7,7’-tetrakis(N,N-dimethoxyphenylamino)-9,9’-spirobifluorene) or PTAA (poly-[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]). Since this work focuses primarily on the characteristics of the HTM—perovskite interface, discussion is limited to that portion of the device.

For high-efficiency perovskites, there are requirements for good alignment with the perovskite structure. One of the such quantities is the relationship of open-circuit voltage losses with interfacial losses at the HTM—perovskite interface. Additionally, it has been noted that the recombination of holes in the HTM and electrons within the perovskite are the main source of recombination losses, and hence charge separation
techniques must be considered [46]. Other parameters to consider is the electronic structure of the perovskite compared to that of the HTM, where a large offset of the valence band in the perovskite and the Highest Occupied Molecular Orbital (HOMO) of the HTM decreases the $V_{oc}$ via hole transport losses [2]. A related notable consideration is the proximity of the Fermi energy of the perovskite in relation to the HTM.

2.3 Use of Thiol Monolayers in MAPbI$_3$

Recently several groups have attempted to utilize self-assembled monolayers to improve solar cell performance and stability. Some of the benefits of using a self-assembled monolayer is the introduction of a dipole at the interface, band-bending and changes to the work function, and other effects on electronic structure [31] [46]. In particular the work of Cao et al. [10] focused on surface modification of the perovskite on the ETL and HTL contacts. Within the HTL—perovskite interface, a highly hydrophobic monolayer, 2,3,4,5,6-pentafluorobenzenethiol, was deposited to increase the environmental stability and observe the impact on PCE. We opt to examine Figure 8: Monolayer used in between the perovskite and HTM in the work by Cao et al. [10], and the molecule used in this work.

![Chemical structure of 2,3,4,5,6-pentafluorobenzenethiol](image)

2,3,4,5,6-pentafluorobenzenethiol

the adsorption of the monolayer on the surface of MAPbI$_3$ using density functional theory, and assess the stereochemistry of adsorption when MA$^+$ orientation may alter
the surface states and thus solar cell performance.
3 Methods

3.1 Density Functional Theory

Density functional theory is used to study these systems using an *ab initio* or *first principles* approach. It has been repeatedly shown that computational methods can describe complex phenomena and physical properties of various systems [11] [23] [37] [43]. This can be understood by the way in which most of these results are obtained - use of clever approaches to approximate solving the many-body Schrödinger equation. The time-independent many-body Schrödinger equation is shown in Eq. (1) below.

\[ \hat{H} \Psi(\{r_i\}, \{R_I\}) = E \Psi(\{r_i\}, \{R_I\}). \]  

(1)

In this equation, \( \hat{H} \) is the hamiltonian operator, \( \Psi \) is the wave function describing the \( n + I \) electrons and nuclei respectively, \( R \) and \( r \) are position vectors for the nuclei and electrons respectively, and \( E \) is the energy of the system. Solving this equation yields insight to the most stable state of a given system. While such an equation appears simple, only hydrogenic atoms are solvable as it is a two-body problem. One method of simplifying the equation is to step away from the nuclei of the system. This is done by employing the Born-Oppenheimer approximation, since nuclei are heavier and “slow” \( 10^{-12} \) s compared to the timescale of electronic events \( 10^{-15} \) s [57]. This allows for one to remove the \( \{R_I\} \) from both sides of the equation, and perform the action of the hamiltonian onto only the \( N \) electrons. Once the
hamiltonian operator $\hat{H}$ is expanded, the result is given as:

$$\left( -\frac{\hbar^2}{2m} \sum_i^N \nabla_i^2 + \sum_i^N V(r_i) + \sum_{i \neq j}^N \frac{q_i q_j}{|r_i - r_j|} \right) \Psi(r_1, \ldots, r_N) = E\Psi(r_1, \ldots, r_N) \quad (2)$$

In Eq. (2), $-\frac{\hbar^2}{2m} \sum_i^N \nabla_i^2$ corresponds to the kinetic energy contribution where $\hbar$ is Planck’s constant divided by $2\pi$ and $m$ is the mass of $i$, and $\nabla^2$ is the gradient with respect to the positional vector, $\sum_i^N V(r_i)$ is the sum of local potentials, and $\sum_{q_i \neq j}^N \frac{1}{|r_i - r_j|}$ is the sum of the coulombic interactions (i.e. electron-electron interactions). At this point, the act of finding a simultaneous solution for all $\{r_i\}$ is an arduous task, and hence one instead maps the complete wave function onto the set of single electron wave functions.

$$\Psi(r_1, \ldots, r_N) \mapsto \{\psi_i(r)\} \quad (3)$$

In Eq. (3), instead of needing to realize simultaneously the positions of all electrons, consideration is made to the set of individual electrons, whose $i^{th}$ wave function is denoted as $\psi_i$ with position vector $r$ [32]. Hohenberg, Kohn, and Sham then proved that it is possible to simplify this expression further [15] [24]. Beginning with calculation of the electronic density, $\rho$, it is computed by taking the expectation values of all of the single electron wavefunctions $\psi_i$ [32].

$$\rho(r) = \sum_i^N |\psi_i(r)|^2 \quad (4)$$

At the heart of Density Functional Theory (DFT) is the Kohn-Sham equation, Eq. (5).

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_Z(r) + V_H[\rho](r) + V_{XC}[\rho](r) \right) \psi_i(r) = \epsilon_i \psi_i(r) \quad (5)$$
In Eq. (5), brackets indicate performing a functional operation (a function acting on a function), $V_Z$ are the interactions of the nuclei onto the electron, $V_H$ is the Hartree potential, the interaction of the electron density $\rho$ with the electron, $V_{XC}$ is the exchange-correlation potential and $\epsilon_i$ are the eigenvalue energy solutions for the single electron. The Kohn-Sham equation clarifies the naming of DFT, since it is the application of functionals onto the density of electrons. The most notably different term in Eq. (5) opposed to Eq. (2) is the exchange-correlation potential, which can be described as a result of interactions of different spin-states of electrons that have some interaction on the wave function [41]. A more mathematically rigorous definition of $V_{XC}$ is the functional derivative of the total exchange-correlation energy, $E_{XC}$ with respect to the electronic density.

$$V_{XC}(r) = \frac{\delta E_{XC}[\rho]}{\delta \rho}$$

(6)

It can also be shown that total energy is uniquely given as a functional of the density [15].

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{XC}[\rho] + E_Z[\rho] + U[Z]$$

(7)

In Eq. (7), $T_s[\{\psi_i[\rho]\}]$ is the kinetic energy of a non-interacting system, $E_H[\rho]$ is the Hartree energy, $E_Z[\rho]$ is the interaction of the electronic density with the nuclei, and $U[Z]$ interaction of nuclei with other nuclei. Solving for the total energy of a given system now has the following unknowns: the descriptor for the single electron wave functions, ($\psi_i$), the energy for the single electron, ($\epsilon_i$), which in turn depend on $\psi_i$ indicating self-consistency, $V_{XC}$ and $E_{XC}$. When iterative minimization techniques are employed to estimate the energy from Eq. (7), the electronic ground state is determined for a set of stationary $\{R_I\}$ nuclei. In the instance the forces on the nuclei (or ions) is still large, by gradually moving the positions of the nuclei based on
the magnitude of these forces, the system may relax the atomic stresses.

When attempting to approximate this unknown exchange-correlation functional, various approaches have been considered. These different approaches are typically in the form of Generalized Gradient Approximations (GGAs), and the Local Density Approximation (LDA) and extend to more complicated hybrid-GGAs that include Hartree-Fock exchange, meta-GGAs and hyper-GGAs that require more memory and gradient calculations [32]. The LDA assumes the form of a homogenous electron gas [24], where the energy contribution for exchange correlation for a single electron at a point \( \mathbf{r} \) is the same as the exchange correlation in a homogenous electron gas with the same density as the electron gas at point \( \mathbf{r} \) [41].

\[
E_{XC}[\rho] = \int \epsilon_{XC}(\mathbf{r})\rho d\mathbf{r}
\] (8)

In general, additional terms in the exchange correlation energy calculation may include other operations acting on \( \rho \) such as the derivative and/or gradients within the integral [32].

After calculating an approximation for the exchange correlation energy and the Kohn-Sham equation, the last necessary key to solving for the ground state energy is a basis set of functions to express \( \psi_i \). For hydrogenic atoms, this is a more-or-less simple choice of solutions to the spherical harmonics [57], but for many other systems, plane waves are the chosen function [41]. For crystalline systems, it is reasonable to enforce periodic boundary conditions, or translational invariance, on the unit cell and Bloch theorem allows for this. The Bloch theorem states that within a periodic solid, each electronic wave function can be understood as the product of a cell periodic part and a wavelike part.

\[
\psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}}
\] (9)

In Eq. (9), \( u_{nk}(\mathbf{r}) \) represents the cell period component of the \( n_{th} \) band index corre-
sponding the Bloch vector \( \mathbf{k} \). In practice, \( n \) is on the order of the number of electrons in the system, and \( \mathbf{k} \) is usually confined to the first Brillouin zone [41].

A key observation is that the larger the real space vector, the smaller the reciprocal space vector, which will be important when performing calculations on slabs with vacuum layers. Moreover, by performing Fourier analysis on the cell periodic components, \( u_{nk}(\mathbf{r}) \), it is possible to rewrite the wave functions in terms of the plane wave basis [32].

\[
u_{nk} = \frac{1}{\sqrt{\Omega}} \sum_G c_n G_k e^{iG \cdot r}
\]

Here, \( \Omega \) is a normalization factor equal to the volume of the Bravais lattice \( h \). Combining Eq. (9) and Eq. (10) yields the wave function as an expansion of the plane wave basis set [41].

\[
\psi_{nk} = \frac{1}{\sqrt{\Omega}} \sum_G c_n G_k e^{i(G + k) \cdot r} 
\]

A consequence of performing this action is there is an infinite set of planewaves that describe a particular system. Fortunately, in practice this can be controlled by an aptly named cutoff energy, \( E_{\text{cutoff}} \). The cutoff energy allows for one to set an upper bound to the planewave energy, given in Eq. (11). This reduces the number of planewave basis functions from infinity to those that satisfy the cutoff energy. This can introduce issues while attempting to solve for dense electronic structures (e.g. near core electrons, tightly bound states, etc.) and hence controlling the overall accuracy for the basis set [32]. This also allows for ease of calculating the density, which is performed by integrating over the first BZ.

\[
\rho(\mathbf{r}) = \frac{1}{\Omega_{BZ}} \sum_n \int_{BZ} f_{nk} |\psi(\mathbf{r})|^2 d\mathbf{k}
\]

By making the approximation that the wave functions at Bloch vectors, \( \mathbf{k} \), are sufficiently close together at special \( \mathbf{k} \)-points [36], the density calculation becomes simplified. By utilizing the \( \mathbf{k} \)-points, the integration can be approximated as a weighted
sum of the discrete set of $k$-points. Symbolically:

$$\rho(r) = \frac{1}{\Omega_{BZ}} \sum_n \int_{BZ} f_{nk}|\psi(r)|^2 dk \approx \sum_{nk} w_k f_{nk}|\psi(r)|^2 dk$$

where the weight values for each of these $k$-points is determined by the choice of $k$-point density, or mesh, and the symmetry of the underlying crystal system. Reduction of the first BZ to the Irreducible Brillouin Zone (IBZ), potentially decreases the total number of calculations required, as symmetric $k$-points will be equivalent. This can be observed in Fig. 9 below.

![Figure 9: Demonstration of symmetry in the first Brillouin Zone for a 4 × 4 $k$-point mesh, where symmetric $k$-points are colored accordingly. Weighting factors of $w_i = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{2}\right)$ for $k_1$, $k_2$, and $k_3$ respectively.](image)

In the above example, the calculation would be dramatically reduced from having to calculate at all 16 $k$-points compared to only having to calculate at three distinct $k$-points and applying the respective weighting coefficients [32].

In summary, there are some calculations that are best performed in reciprocal space versus real space. Interconversion of the Fourier coefficients of $G$ to $h$ is performed by a Fast Fourier Transform (FFT), which scales with $\mathcal{O}(n_{FFT}) = n_{FFT}\log n_{FFT}$ where $n_{FFT}$ is the number of grid points for the FFT.

Finally is the introduction of pseudopotentials, and in particular, the Projector
Augmented Wave (PAW) method. As previously discussed, $E_{\text{cutoff}}$ has a large impact on the accuracy of the DFT calculation, and for plane wave basis sets, tightly bound states and especially core electrons have dramatically larger interactions and energies than that of outer shell electronic densities. To account for this, pseudopotentials can be used to decrease the necessary size of the plane-wave basis set [41]. The approximation performed consists of the removal the core electrons, replacement with a weak pseudopotential (often based on spherical harmonics for quantum numbers $m$ and $l$) which allows for weak pseudo-wave functions to interact with them.

Figure 10: Detailing the all-electron wave function, $\psi_v$, and potential compared to the pseudo alternative. At a particular cut-off radius, $r_c$, the wave function, and potential and their respective pseudo- counterparts are equal. Adopted from [41]

In this study, the PAW method is used to envelope the local potential of the ions (the highly oscillatory region) to a specific cut-off radius, then use the plane waves to describe the space at and beyond said cutoff radius. The particular strategy for PAW was first described by Blöchl [7] and is incorporated into the software used for this research: the Vienna ab initio Simulation Package (VASP) [26] [27] [28]. While there are many more intricacies in this particular software package, from the Kohn-Sham equations, it is possible to generate a set of wave functions that are capable
of mapping the many-body Schrödinger equation. These wave functions for the set of
atoms, as defined by the user, can then be optimized via energy minimization. Forces
then are calculated on the ions, and the program can move them (unless otherwise
specified), and the optimization can conclude depending on the maximal force on
ions, or change of energy from one configuration of ions to the next.

3.2 Optimization of Bulk Perovskite

All of the following ab-initio calculations were performed using the Vienna ab initio
Simulation Package [26] [27] [28]. From results garnered from previous students’ work
[5] [40], a previously available file for a volumetrically relaxed MAPbI$_3$ cell was used
as a baseline for the next set of simulations. To verify this structure was optimized,
the calculation allowed for the ions to move until the forces on the nuclei was less
than 0.01 eV/Å. For all calculations a cutoff energy of 600 eV was used. Usage of the
GGA for the exchange-correlation was that of Perdew, Burke, and Ernzerhof revised
for solids (PBEsol) [11] and energy corrections for van der Waals interactions were
included using the built-in code provided by Klimeš, Bowler and Michaelides [23].
A Monkhorst-Pack $k$-point mesh of $3 \times 3 \times 2$ was utilized [36]. After optimization,
locations for the atoms were verified using the anisotropic displacement parameters
(ADPs), bond lengths, and lattice constants [54] [44] [8]. Since convergence analysis
for the lattice constants was previously performed [5], the addition of volumetric
relaxation (ISIF = 3) was deemed redundant and was not performed.

3.3 Extraction and Embedding of Methylammonium Moi-
eties

Once the baseline structure was obtained, MA$^+$ positions for experimental struc-
tures were needed. Two .cif files were obtained from experimental works from Stoumpos
et. al [54], and Ren et. al [44]. By loading these files into the Visualization for Electronic and STructural Analysis [35] (VESTA) program, exact positions for the MA$^+$ ions were extracted. Then, the structure S was generated with the corresponding MA$^+$ positions from Stoumpos et al., but retained the PbI$_6$ octahedra from our previous work. Similarly the structures from Ren et al. included four-fold degenerate locations for nitrogen in each “site” within the perovskite, each of these orientations was isolated in a separate structure, and the other MA$^+$ ions were oriented parallel to these four positions. This generated the family of R structures, R-I, R-II, R-III, and R-IV. The atomic coordinates for these ions were removed from the corresponding .cif files and introduced to the lead-iodide framework from the previous step. To optimize these structures, a two-step process was performed, initially relaxing the maximum forces on ions to 0.05 eV/Å, then to 0.01 eV/Å. Each time, a Monkhorst-Pack $k$-point mesh of $3 \times 3 \times 2$, Gaussian smearing ($\sigma = 0.1$), and a conjugate gradient routine was used in the ionic relaxation, and the ions were allowed to move but the volume of the unit cell remained fixed.

3.4 Generation and Relaxation of C$_6$F$_5$SH

The structure of the monolayer C$_6$F$_5$SH was initially made using GaussView 6. This software allows for easy generation of molecules and has a variety of useful formats for exporting atomic coordinates. After generating these coordinates, the molecule was centered within a 20Å $\times$ 20Å $\times$ 20Å box to disallow the forces of periodic images from interacting with itself. Another main modification of the simulation was having $k$-point sampling only at the $\Gamma$ point due to the cell being non-periodic [32]. Additionally, $\sigma$ was set to 0.01 due to the finer electronic structure of the organic molecule, and the atomic positions were optimized using a conjugate gradient routine until the forces on the ions were less than 0.01eV/Å.
3.5 Generation of Perovskite Slabs

Following a similar analysis to Geng et al. [12], 1 × 1 × 2 supercells were created for each of the two distinct surfaces – one with MAI on top, and one with PbI on top. Having eight distinct alternating atomic layers, the bottom four layers were set to be fixed using selective dynamics, and the top four layers were allowed to move. Then, 20Å of vacuum was placed over the free layers in the c direction, to allow for surface relaxation. To optimize these structures, a two-step process was performed, initially relaxing the maximum forces on 'free' ions to 0.05 eV/Å, then to 0.01 eV/Å. A Monkhorst-Pack $k$-point mesh of $3 \times 3 \times 1$ was used for these slabs, Gaussian smearing ($\sigma = 0.1$) was included, and a conjugate gradient routine were used in the ionic relaxation, and the ions were allowed to move but the volume of the unit cell remained fixed.

3.6 Placement and Optimization of C$_6$F$_5$SH onto Perovskite Surfaces

When each of the slabs was optimized, three high-symmetry locations were chosen for each MAI and PbI slabs for the monolayer to absorb onto. For each of these positions, the position of the sulfur atom was placed such that the likelihood chemisorption and physisorption were equivalent. This was done via Eq. (14)

$$d_m \approx \frac{1}{2} (r_{vi}^{vdw} + r_{vj}^{vdw} + d_{cov}^{S-j}) \forall j_b$$

subject to $z_S \geq z_{slab}$ (14)

where $d_m$ is the requisite distance for the monolayer to be placed away from the bonding species $j$, $r_{vi}^{vdw}$ is the van der Waals radius for the species $i$ as presented by Batsanov [6], and $d_{cov}^{S-j}$ is the $\sigma$-bond length of S-$j$ bond as provided by Allen et al. [3]. When multiple bonding sites were possible (as with the ”hole” positions), Eq. (14)
was applied for all possible bonding atoms, while keeping the initial sulfur position at or above the topmost atom in the slab.

The sites for the PbI on top slabs were directly over the top-most lead atom, as reported in other works [10] [31], overtop the top-most iodine, and within the ‘hole’ on the PbI surface. To parallel, for the MAI on top slabs, the sulfur was placed over the topmost iodine, the topmost carbon in MA$^+$, and within the hole in the perovskite surface. The positioning of the monolayer in each of these slabs was within the 20Å vacuum layer from the previous set of slab simulations. To optimize these structures, a two-step process was performed, initially relaxing the maximum forces on ‘free’ ions to 0.05 eV/Å, then to 0.01 eV/Å. A Monkhorst-Pack $k$-point mesh of $3 \times 3 \times 1$, Gaussian smearing ($\sigma = 0.1$), and a conjugate gradient routine was used in the ionic relaxation, and the ions were allowed to move but the volume of the unit cell remained fixed. Once these structures were generated, it was possible to interpret adsorption energy $E_{\text{ads}}$, for a single monolayer on a $1 \times 1 \times 2$ supercell, which can be determined via Eq. (15).

$$E_{\text{ads}}^o = E_{g,\text{slab+mono}}^o - E_{g,\text{slab}}^o - E_{g,\text{mono}}^o$$ (15)

Here, we employ the ground state energies that were determined in the previous steps yielding insight of the relative stability of the modified slab and generate the adsorption energy. The more negative $E_{\text{ads}}$ is, the more energetically favorable the monolayer absorption is, while positive values are thermodynamically unfavorable. In order to understand the stabilization that occurs when the monolayer and slab are in a frustrated state, it is possible to freeze the atomic positions and artificially separate the slab from the monolayer. A single self-consistent field calculation is performed to yield these non-standard energies, and comparison is made from the “frustrated slab” with the monolayer artificially removed and $E_{g,\text{slab}}^o$. 

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3.7 Charge Density Analysis and Density of States

Once the slab+monolayer constructs (modified slabs), were relaxed, several analyses were performed to check the impact on the electronic structure of the modified slab. Particular interest was in the charge density difference of the modified slab and its substituents to see how the slab may stabilize the monolayer, or vice-versa. Charge density difference plots are generated by taking the difference of the charge density, $\rho$ for the modified slab and the sum of the constituents as seen in Eq. (16).

$$\Delta \rho = \rho_{\text{slab+mono}} - \rho_{\text{slab}} - \rho_{\text{mono}}$$ (16)

In VASP, this is possible by decomposing the modified slab back into the monolayer and slab, and then running a Self-Consistent Field (SCF) loop or a static calculation where the atoms are not allowed to move. This yields information regarding the redistribution of charges, i.e. charge accumulation and charge depletion, which can also give insight into the bonding within the system. This static calculation can yield more information which involves output of the $lm$-decomposed density of states, and the local potential. In order to visualize these, data is extracted and cleaned using VASPKit [59], and plots are made using GNUplot.

3.8 Use of the Detailed Balance Limit

The detailed balance limit originally derived by Shockley and Queisser allows for tremendous simplification of the processes within a photovoltaic device. Within the detailed balance derivation, the most convoluted step is the treatment of charge carrier dynamics. Five processes are considered in the SQ derivation: 1) the rate of photogenerated hole-electron pairs, 2) radiative recombination of hole-electrons due to resultant photoemission, 3) non-radiative processes which generate hole-electron pairs which reside in thermal equilibrium with the cell 4) non-radiative processes that
eliminate hole-electron pairs are reduced to zero, and 5) removal of holes in p-type areas and electrons in n-type areas due to some current or idealized separation of charges. In the steady state, the sum of these processes should be equal and thus “balanced” [52].

The derivation begins considering the total available photonic energy usable for the system. For a given spectrum (i.e. Fig. 6) in terms of spectral irradiance, the total incident photon flux on a given area $\phi^i$ can be ascribed as the following.

$$\phi^i = \frac{q\lambda}{hc} * \text{spectrum} \left( \frac{W}{m^2nm} \right)$$  \hspace{1cm} (17)

In Eq. (17), $q$ is the elementary charge, $\lambda$ is the wavelength, $h$ is Planck’s constant, and $c$ is the speed of light in vacuum. For the Shockley-Qiessier limit, a black body emitting at 6000 K is used to emulate the solar spectrum, while for the present study, the AM 1.5G spectrum is used for comparison. This is due to the relevance as compared to experimental measures of solar cell performance metrics and has been well tabulated by [47].

Then considering a p-n junction with an energy gap $E_g$, at an operating temperature of 25°. Assuming for all photons with energy $E$ that meet or exceed $E_g$, the photon is capable of generating a single hole-electron pair, whereas all photons with energies less than $E_g$ are non-interacting with device, the absorption as a function of energy, $a(E)$, is a step function. It is then possible to write the maximum photocurrent density, $J_{max}$ as

$$J_{max} = \int_{0}^{\infty} a(E)\phi^i(E)dE = \int_{0}^{E_g} 0 * \phi^i(E)dE + \int_{E_g}^{\infty} \phi^i(E)dE. \hspace{1cm} (18)$$

Since within the detailed balance limit, the carrier lifetimes are assumed to be infinite until radiative recombination, and the sample is pristine such that only radiative recombination is the only pathway available i.e. external photon emission. This
can then be generalized to generate the emitted photon flux $\phi^e$ as a function of an externally applied voltage due to quasi-Fermi level splitting, $V$ and photon energy $E$.

$$
\phi^e(E, V) = \frac{2\pi E^2}{h^3 c^2} \frac{a(E)}{e^{\frac{E-qV}{k_B T_C}} - 1}
$$

(19)

On the right-most side, is the Bose distribution relating to the fermi splitting at operating temperature of the cell, $T_C$, $k_B$ is Boltzmann’s constant. Following a similar integration yields a quantity, $J_r$, the radiative recombination current density. It also must be considered that the photon emission in the simplest model is where photons can exit through the back and front of the device. Hence, Shockley and Queisser assign a geometric factor, $f_g = 2$ to allow for this phenomenon.

$$
J_r(E_g, V) = f_g q \int_0^\infty \frac{2\pi E^2}{h^3 c^2} \frac{a(E)}{e^{\frac{E-qV}{k_B T_C}} - 1} dE = \frac{4q\pi}{h^3 c^2} \int_{E_g}^\infty \frac{E^2}{e^{\frac{E-qV}{k_B T_C}} - 1} dE
$$

(20)

Now, considering the steady state external current density, $J_{ext}$, the sum of all processes.

$$
J_{ext} = J_{max} - J_r(V) + J_{nr}(0) - J_{nr}(V)
$$

(21)

In Eq. (21), $J_{nr}(0)$ represents the non-radiative generative processes, and $J_{nr}(V)$ represents the non-radiative recombination processes. In accounting for the net generation of carriers that results from the cell at a blackbody temperature, $T_C$, it is instructive to group these terms. Hence, Eq. (21) is equivalent to Eq. (22), but the bracketed values are due to the cell being exposed to a blackbody at $T = T_C$.

$$
J_{ext} = J_{max} - J_r(0) + [J_r(0) - J_r(V) + J_{nr}(0) - J_{nr}(V)]
$$

(22)

In deriving the values commonly reported for solar cell efficiencies, one metric is then the short circuit current, $J_{sc}$, which is the current generated due to the generation of hole-electron pairs via sunlight, less those generated by thermal recombination at 0
\[ J_{sc} = J_{max} - J_r(0) \]  

(23)

To then calculate the open circuit voltage, one minimizes \( J_{ext}(V) \), and that corresponding voltage is the open circuit voltage. In determining the maximum power voltage, the product of \( V_{oc} \) and \( J_{ext}(V) \) is then maximized. In a similar treatment, \( J_{mpp} \), the current density at the max power point, is corrected by the recombination density at \( V_{mpp} \).

\[ J_{mpp} = J_{max} - J_r(V_{mpp}) \]  

(24)

The max power output for the device is then calculated by Eq. (25)

\[ P_{max} = J_{mpp} V_{mpp} \]  

(25)

Which can then easily be related to the maximum theoretical efficiency (PCE or \( \eta \)) by dividing \( P_{max} \) by the integral of the entire solar irradiance spectrum. For the ASTM 1.5G spectrum, this corresponds to a power density of 1000 W/m\(^2\) [47].
4 Results and Discussion

4.1 Comparison of Initial Structure with Literature

Beginning with the initial structure that was previously relaxed, we compare the crystallographic properties with those found in literature.

Table 1: Comparison of our initial bulk structure \textbf{I} crystallographic properties with those for MAPbI$_3$ in the tetragonal phase found in literature.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$\angle_i^c$ (°)</th>
<th>$\angle_i^{ab}$ (°)</th>
<th>PbI$_c$ (Å)</th>
<th>PbI$_{ab}$ (Å)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>T (K)</th>
<th>method</th>
</tr>
</thead>
</table>

In Table 1, lattice constants, experimental methods, and, where necessary, indication of temperature are noted. Superscripts are used to indicate the plane the bond angle or bond length spans. For measurement of the angles in particular, the angle measured corresponds to Pb-I-Pb bonds in the $c$ and $ab$ directions. As seen in Table 1, there appeared to be rather dramatic differences in specifically the bond angles and lengths in \textbf{I} compared to those determined experimentally. To verify that the results garnered for the bulk structure were reasonable, the .cif files provided by Stoumpos et al., and Ren et al., were further investigated.

In concurrence with the International Union of Crystallography, atomic displacement parameters (ADPs) for the XRD and ND data were given for each experimental
dataset. ADPs allow for insight into the experimental and atomic uncertainties that may be present within the system such as thermal motion, or other displacive disorder. Since diffraction techniques involve the interaction of an X-ray/neutron with the electronic/neutron density, the measurement is taken from the reflection and hence the diffraction pattern is generally gaussian in appearance [56]. VESTA allows for generation of these atomic displacement ellipsoids, which depend on the isotropic displacement parameter $U_{iso}$ or anisotropic displacement parameter $U_{ij}$, and the percent likelihood. When the ADPs are treated isotropically, the atomic displacement parameters are spherical which is approximately a uniform ‘variance’ in the x,y and z coordinates for a particular atomic coordinate. The anisotropic variant may have differing ‘variances’ in each of the directions, which results in a more accurate ellipsoidal appearance. Intuitively, the larger the percent likelihood, the larger the displacement ellipsoids are. The larger the atomic displacement parameter, the larger the ellipsoid will also be for equivalent likelihood values. This is distinctly shown in Fig. 11(a), where the reported ADPs for carbon and nitrogen are much larger than those for iodine and lead.
Figure 11: a) Anisotropic displacement ellipsoids from Stoumpos [54](transparent) with 50% probability and the atomic positions from relaxed I(opaque). Hydrogen atoms not shown. b) Figure indicating the difference Fourier mapping of positive neutron scattering, displacement ellipsoids for I drawn at 50% probability, adopted from Ren et al. [44].

As seen in Fig. 11a), the ADPs provided for carbon and nitrogen from Stoumpos et al. [54] are very large which arise from experimental limitations using XRD as the interacting cross-section scales with the atomic number, Z, and due to MA⁺ reorientation [42]. In Fig. 11b), the positive Fourier mapping of scattering from neutron diffraction can be interpreted as the summation of carbon and nitrogen neutron density, which indicates a clear disorder within these sites. Each of these sites allow for a four-fold degenerate structure, which allowed for generation of four separate parallel orientations from the Ren structures. Since significant overlap occurred with our previously obtained structure when superimposed with the ADPs, we proceeded with embedding the MA⁺ structures from these two works within the PbI₃ backbone from our initial structure I.
4.2 Generating Bulk Structures

Once the MA$^+$ ions were embedded into the $\text{IPbI}_3$ framework, five structures were generated with each unit cell containing 48 atoms ($\text{(CH}_3\text{NH}_3\text{PbI}_3)_4$). Each structure was made such that the orientation of the MA$^+$ ions were parallel, though in the “Ren” analogues, the top and bottom methylammonium species will appear flipped due to the inversion symmetry. Upon successful optimization via relaxation of forces acting on ions, the bulk structures in Fig. 12 resulted. It is noted here that the dangling iodine atoms are redundant, but are shown to illustrate the PbI$_6$ octahedra present in the perovskite crystal structure.

![Bulk Structures](image)

Figure 12: Depicting each of the MA$^+$ orientations within the bulk structures. In this and subsequent figures, iodine is represented by purple spheres, lead in gray, nitrogen in blue, carbon in brown and hydrogen in white.

Here it is possible to declare the approximate orientations of the methylammonium
ions within the PbI₆ framework: S is [001], R-I is [110], R-II is [110], R-III is [110], and R-IV is [110]. Each of the R structures have a visually uniform and straightened PbI framework, while the S structure retains more of the tilted state.

Since the lattice constants were held fixed, comparison between the bond lengths and bond angles are possible, as well as the energy difference between the most stable structure (determined to be S). These are tabulated in Table 2.

Table 2: Comparison of the ground state energy of the bulk structures, rounded to nearest meV. Minimum energy structure indicated with †

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\angle c_I$ (°)</th>
<th>$\angle a_I$ (°)</th>
<th>(PbI^c) (Å)</th>
<th>(PbI^ab) (Å)</th>
<th>(E - E_{min}) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S†</td>
<td>174.28</td>
<td>155.13</td>
<td>3.245</td>
<td>3.199</td>
<td>0</td>
</tr>
<tr>
<td>R-I</td>
<td>176.24</td>
<td>154.20</td>
<td>3.141</td>
<td>3.236</td>
<td>28</td>
</tr>
<tr>
<td>R-II</td>
<td>176.73</td>
<td>153.58</td>
<td>3.124</td>
<td>3.205</td>
<td>26</td>
</tr>
<tr>
<td>R-III</td>
<td>178.83</td>
<td>153.90</td>
<td>3.121</td>
<td>3.222</td>
<td>25</td>
</tr>
<tr>
<td>R-IV</td>
<td>177.87</td>
<td>155.78</td>
<td>3.132</td>
<td>3.249</td>
<td>35</td>
</tr>
</tbody>
</table>

As shown in table 2, the Pb-I-Pb bond angle in the c direction appears to straighten and match more closely with the results garnered from experimental works. It is important to note that the lattice parameters are the same as those used for structure I, and for reference are in table 1.

4.3 Band Gap and Fermi Energies of Bulk Structures

In order to determine the impact of the surface states via reconstruction as opposed to the bulk structure, the density of states of the bulk for each structure was generated. After each of the bulk structures were fully relaxed, a static calculation was run, with the only modification to the default settings being the increase of the number of gridpoints the DOS is calculated (NEDOS) was increased to 3001 (from 301). In Fig. 13, the projected DOS for S is shown.
In Fig. 13 the DOS are quite jagged which is expected to arise from small broadening used to show details. Near the Fermi energy most of the valence band consists of I(5p) and slightly Pb(6s) states and the conduction band maintains Pb(6p) and I(5p) character. Calculating the bandgap for this system by taking the closest direct gap at any k-point is 1.892 eV (at the Γ-point). Comparing this value to Rühl’s table of values [47], the theoretical maximum $J_{mpp}$ is $16.92 \text{mA/cm}^2$, $V_{mpp}$ is 1.475V, and the maximum PCE is 24.96% for a p-n junction with this bandgap. Similar structure is seen in the first of the R structures as seen in Fig. 14.

For R-I, the DOS appears visually the same, and near the Fermi energy most of the valence band consists of I(5p) and Pb(6s) while the conduction band maintains Pb(6p) and I(5p) character, consistent with the last results. Calculating the bandgap for this system by taking the closest direct gap at any k-point is 1.991eV (at the Γ-point), a hypsochromic shift by 36meV. Comparing this value to Rühl’s table of values [47], the optimal $J_{mpp}$ is $14.57 \text{mA/cm}^2$, $V_{mpp}$ is 1.567V, and the maximum PCE is 22.84%. The remainder of DOS plots for the R family of bulk structures can be found in the appendix as they were found to be visually similar to R-I and S. These results
Figure 14: (Left) Elemental Projected Density of States and (Right) lm-decomposed PDOS for bulk R-I. These plots have been shifted such that $E_{\text{Fermi}} = 0$.

have been tabulated in table 3. In order to compare the proximity of the gap of the bulk structures to those reported experimentally, two experimental results have also been included in the table.

Table 3: Values for the bandgap and theoretical maximum solar cell performance of each of the bulk structures using the detailed balance limit as suggested by Rühle [47]. These operating conditions assume AM 1.5G illumination and an operating temperature of 25°C.

<table>
<thead>
<tr>
<th>Bulk</th>
<th>$E_g$ (eV)</th>
<th>$J_{mpp}$ (mA cm$^2$)</th>
<th>$V_{mpp}$ (V)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1.892</td>
<td>16.92</td>
<td>1.475</td>
<td>24.96</td>
</tr>
<tr>
<td>R-I</td>
<td>1.991</td>
<td>14.57</td>
<td>1.567</td>
<td>22.84</td>
</tr>
<tr>
<td>R-II</td>
<td>2.033</td>
<td>13.71</td>
<td>1.604</td>
<td>21.98</td>
</tr>
<tr>
<td>R-III</td>
<td>2.034</td>
<td>13.71</td>
<td>1.604</td>
<td>21.98</td>
</tr>
<tr>
<td>R-IV</td>
<td>2.003</td>
<td>14.35</td>
<td>1.577</td>
<td>22.62</td>
</tr>
<tr>
<td>MAPbI [48]</td>
<td>1.59</td>
<td>25.28$^\dagger$</td>
<td>1.200$^\dagger$</td>
<td>30.33$^\dagger$</td>
</tr>
<tr>
<td>MAPbI [2]</td>
<td>1.60</td>
<td>24.94$^\dagger$</td>
<td>1.209$^\dagger$</td>
<td>30.14$^\dagger$</td>
</tr>
</tbody>
</table>

$^\dagger$- Emphasizes these are theoretical values for the given bandgap.
It is also worth indicating that the calculated bandgaps are similar to those with the same level of theory in DFT studies [17] [37] [4]. To better illustrate this point, several values from other works have been shown in Fig. 15.

Figure 15: Comparison of different perovskite compositions (MAPbX$_3$) and their respective bandgaps as calculated using various methods. This work focuses exclusively on tetragonal MAPbI$_3$, and the range of garnered values are indicated in yellow. Figure adopted from Melissen et al. [33].

Mismatch in the bandgap can arise from a lack of an incomplete descriptor of the exchange-correlation, which may be remediated by a more precise description (i.e. the use of m-GGA methods, hybrid functionals) with large added costs of computational complexity. Other factors that could generate this result is the result of lack of consideration of spin orbit coupling and resultant Rashba splitting [34]. Heavy atoms, such as Pb and I, are renowned for causing relativistic effects such as the “heavy-atom effect”, which may shift the direct bandgap off of the Γ-point [57].

4.4 Creation of Slabs

After successful generation of these relaxed bulk structures, $1 \times 1 \times 2$ supercells were created, and the top four layers were exposed to a 20Å vacuum. The top four layers were allowed to relax, while the bottom four layers were fixed. To consider
the effects of monolayer absorption on both the MAI terminated and PbI terminated slabs, it was necessary to create two separate slab structures for each of these cases. To better illustrate the procedure, Fig. 16 shows the full height of the cells, and indicates the specified layers within the cell.

![Illustrating the fixed layers (1 through 4, directed with arrows in black) and the free layers (5 through 8, directed with arrows in red) for MAI terminated S and PbI terminated S. These slabs have already been optimized.](image)

Figure 16: Illustrating the fixed layers (1 through 4, directed with arrows in black) and the free layers (5 through 8, directed with arrows in red) for MAI terminated S and PbI terminated S. These slabs have already been optimized.

The entire set of relaxed PbI terminated slab structures are shown below in Fig. 17, while the set of structures for the MAI terminated slabs are shown in Fig. 18. For ease of viewing, the 20Å vacuum has been cropped from these figures.

In Fig. 17, aside from S-P, there does not appear to display significant deformation from the bulk structure (layers 1-4) compared to the surface structure (layers 5-8). In S-P, which energetically is the least stable by 1.595 eV, the cations towards the surface level appear to reorient in the [110] direction, but do not possess the same $S_2$ symmetry operation over the $<110>$ plane as the R structures (i.e. an inversion...
Figure 17: Relaxed PbI terminated slabs. † indicates the most stable configuration.

Other than some expected elongation in the z direction, the remaining structures appear relatively the same, and the relative energy differences are tabulated in Table 4. Due to the nature of the PbI top layer halting some of the possible motion of the MA\(^+\) moieties, additional reorientation at the top of the slabs is observed in Fig. 18.

Particular attention is drawn to structures R-II-M and R-III-M, wherein the surface MA\(^+\) reorients entirely, flipping about its axis and leaving the slab with only methyl groups and iodine facing the vacuum layer. Furthermore, these two structures
are the most energetically stable of the group by approximately 220 meV. The relative energy values for these slabs and the PbI terminated slabs are tabulates in table 4. Similar calculations of the bandgaps of the slabs, as performed for the bulk structures, can be found in the Appendix. It is noted that the MAI terminated slabs were consistently more energetically favorable compared to their PbI counterparts. This is attributed to greater freedom of motion of the topmost layer allowing less restricted cation motion, and potentially greater stabilization of dangling bonds on the bottom of the slabs. Moreover, it requires more energy to break the PbI bond to create a PbI$_2$ terminated surface. This is in agreement with other DFT works following similar methodology [12] [17].

Interested in the dramatically energy difference in the slabs - to further investigate this phenomena, 3D-isosurfaces of charge density were generated for the S-P, R-III-P, S-M, and R-II-M structures. This was done to examine the areas of localized electronic density. This aids in identifying dipoles that may exist within the structure (as with the case of MA) as well as identify possible anomalies within the structures. Figure 19 shows the dipoles of the MA structures within the slabs.

Within Fig. 19, the relative dipoles across each of the structures is shown. This

<table>
<thead>
<tr>
<th>Top Layer</th>
<th>MAI Orientation</th>
<th>$E - E_{\text{min}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbI</td>
<td>S</td>
<td>1595</td>
</tr>
<tr>
<td></td>
<td>R-I</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>R-II</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>R-III</td>
<td>201</td>
</tr>
<tr>
<td></td>
<td>R-IV$^\dagger$</td>
<td>0</td>
</tr>
<tr>
<td>MAI</td>
<td>S</td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>R-I</td>
<td>304</td>
</tr>
<tr>
<td></td>
<td>R-II$^\dagger$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>R-III</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>R-IV</td>
<td>260</td>
</tr>
</tbody>
</table>
Figure 19: Three dimensional charge density plots. Isosurfaces are drawn in white, orange, red, and purple, at 0.2, 0.3, 0.4, 0.5 e/bohr³ respectively.

easily shows the partial negative charge ($\delta^-$) on nitrogen, and partial positive charge ($\delta^+$) for carbon in MA$^+$. As the electron density is more diffuse for lead and iodine, the electronic density is not apparent at these isosurface values. For the lead terminated slabs, the freedom of motion of the methylammonium ions are restricted. For the R-M structures, only two (R-II-M and R-III-M) exhibit reorientation of the MA such that the dipoles align at the surface level. Within the S structures, though, the dipoles align across the length of the supercell which has been suggested to decrease the carrier-lifetimes hindering PCE [29].

The energetic increase can be explained by the energetically unfavorable dipole orientations that must span the vacuum interface. As seen in Fig. 19, there is a partial negative charge on the bottom of the S-P slab by both apparent MA$^+$s, which cannot be balanced by a nearby MA $\delta^+$-carbon. For the case of the R species, which stabilize opposing dipoles via periodically inverted MA$^+$s in the ab directions, the dipole effect is more-or-less stabilized within each layer, which decreases the energy. For R-II-M, only the top-most layer breaks this pattern, and this is ascribed by a net decrease in energy by unrestricted movement of the methylammonium ions at the
surface.

To see if there was modulation of the electronic surface charge of the slabs, more isosurfaces were drawn to show the dipoles and weak electronic density as shown in Fig. 20.

Interestingly the dipole effects do not seem to impart major visible electronic changes in the top and bottoms for each of the slabs with lower charge densities included, which also provides a possible basis for the ergodic motion of the MA$^+$. There are slight differences in the S structures - for the PbI terminated ends, (the top of the slab for S-P and the bottom, frozen part in S-M), there is greater extension of the electronic cloud over/below the iodines. Compared to the R-III-P structure shown, the electronic density is much more level. This may imply that there are different MA$^+$ dipole orientation effects on the lead terminated slabs attributed to a more level electronic surface charge.
4.5 Pentafluorobenzenethiol Optimization

Upon slab relaxation, it was necessary to optimize the structure of pentafluorobenzenethiol, C₆F₅SH.

![Relaxed structure of the monolayer (m), C₆F₅SH](image)

The C-S distance is measured as 1.770 Å, which compared well to the literature value for an aryl-C-S bond (1.773 ±0.009Å) and hence are in agreement [3]. During the relaxation, the pentafluorobenzene group remained planar, which was qualitatively expected. The bond angle, \( \angle S \), between H-S-C₁ was measured to be 96.39° and the dihedral angle of C₂-C₁-S-H was 91.93°. As this structure relaxation was a \( \Gamma \)-point calculation with no smearing, the approximate HOMO and Lowest Unoccupied Molecular Orbital (LUMO) from the eigenvalue solutions were found to be \(-6.600\) eV and \(-2.498\) eV respectively. This corresponds to a HOMO-LUMO energy gap of 4.102 eV, which is consistent with benzenethiol derivatives [31]. While the calculation was not performed, the main degree of freedom should be rotation about the C₁-S axis resulting in movement of the hydrogen, which may lower the total energy of the monolayer. It is possible that a local minima for the atomic configuration (and electronic density) satisfies the same force criteria, but the two positions are not isoenergetic.
4.6 Generation of Modified Slabs

Upon optimization of the monolayer adsorbed onto the slabs, there were significant differences in the energies. Table 5 shows the relative energy differences for each slab, compared to the most stable monolayer placement. The MAI terminated slabs were on average 370 meV more stable than the PbI terminated slabs which is assumed to follow the same energy reduction mechanism in the pristine slabs such as unrestricted cation motion, surface formation energy, and dipole mechanisms.

Table 5: Most stable monolayer positions for each of the slabs.† indicates the reference energy, $E_{min}$.

<table>
<thead>
<tr>
<th>Top Layer</th>
<th>MAI Orientation</th>
<th>Monolayer Position</th>
<th>$E - E_{min}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbI</td>
<td>S</td>
<td>Hole</td>
<td>1640</td>
</tr>
<tr>
<td></td>
<td>R-I</td>
<td>Hole</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>R-II</td>
<td>Over Pb</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>R-III†</td>
<td>Over Pb</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>R-IV</td>
<td>Hole</td>
<td>195</td>
</tr>
<tr>
<td>MAI</td>
<td>S</td>
<td>Hole</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>R-I</td>
<td>Hole</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>R-II†</td>
<td>Hole</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>R-III</td>
<td>Hole</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>R-IV</td>
<td>Hole</td>
<td>25</td>
</tr>
</tbody>
</table>

From these results, four modified slabs were examined in detail, $\text{R-III-P}$, $\text{S-P}$, $\text{S-M}$ and $\text{R-II-M}$. This is also due to similar bonding mechanisms for the family of positions, and asserts that a similar bonding regime should have more-or-less equal impact on electronic structure. For the MAI terminated slabs, it turned out that the minimum energy adsorption geometries for different MA$^+$ orientations all belonged to the initial ‘hole’ position of the monolayer on the surface. For the PbI terminated slabs, since there were two initial positions of the monolayer that heralded the minimum energy, the two positions of ‘Over Pb’ and ‘Hole’ were examined, which offered insight to electronic structure differences and changes in stereochemistry.
4.7 Energetics and Inferences for PbI Terminated Slabs

This subsection is specifically dedicated to the geometry of monolayer adsorption, charge density analysis, local potential analysis and comparison of density of states for the lead terminated slabs.

4.7.1 Geometry of Monolayer Absorption in PbI Terminated MAPbI₃

As depicted in Fig. 22, there is significant change in the monolayer orientation in the monolayer modified slab R-III-P+m.

Figure 22: Monolayer-modified R-III-P+m a) Initial positions b) Magnified view highlighting the difference in positions where the initial positions are greyed out, and the final positions are colorized.

The initial distance between the sulfur of C₆F₅SH and the topmost-Pb of the slab was set at a distance of 3.418Å, as specified in equation Eq. (14). This distance reduced by 0.172Å, resulting in a relaxed Pb⋯S distance of 3.246Å. Further, dramatic reorientation of the monolayer occurred, becoming effectively parallel with the slab surface. The initial angle between C₁-S⋯Pb was nearly vertical, 177.09°, where
after optimization reorients to 90.57°. The initial dihedral angle between C$_2$-C$_1$-S-H was 91.93°, which changes to 123.63° and the sulphyrdal hydrogen orients closer to the surface of the slab, approximately 0.8Å closer than the plane of the remainder of the monolayer. Additionally, the surface of the perovskite remained well preserved; the $\angle_{ab}^{gb}$ angle of linking octahedra at the surface changes slightly from 161.80° to 151.14°. There was also little movement and rotation of the methylammonium ions. This planarization can have a dramatic impact – since the monolayer is 6Å long, it is possible that in this position the monolayer may interact with periodic images of itself. This corresponds to high adsorption density of this particular choice of monolayer, that would need special attention for larger thiols.

Due to this reorientation, it is possible to suggest that such a surface modification may decrease the likelihood of lattice mismatch with HTMs. Similar bulky aromatic structures common to HTMs (such as PTAA, Spiro-OMeTAD, and other high-mobility organic HTMs) may have greater ease of binding to the aromatic $\pi$-systems forming dimer-like interactions [46]. This reorientation may better block other adsorbates that denature the perovskite (i.e. water), and act as a protecting group for temporal longevity. The combination of these two effects should decrease the lattice mismatch and increase overall performance of the solar cell [21]. To contrast, with the orientation of the MA$^+$ in the structure S-P+m, planarization does not occur and an entirely different bonding regime presents, as shown in Fig. 23.

The adsorption mechanism for S-P+m is quite different, where little reorientation of the monolayer occurs and weak secondary bonding dominates. The monolayer moves upward from the center of the hole on the perovskite surface by $\sim$ 0.5Å, and rotates by 17° about the b-axis. The -SH group also rotates about the C$_1$-S bond, changing the C$_2$-C$_1$-S-H dihedral angle from 91.65° to 155.80°. Rotation of the MA$^+$ ions was also present, and the surface of the perovskite deformed close to the monolayer. In particular, the iodine closest to the sulfur moved such that the angle,
Figure 23: Monolayer-modified S-P+m a) Initial positions b) Magnified view highlighting the difference in positions where the initial positions are greyed out, and the final positions are colorized.

$\angle_1^{ab}$, changed from 161.23° to 144.24° once relaxed indicating a more poor match to the perovskite lattice compared to R-III-P+m. This disruption of the perovskite then introduce areas in which opportunistic defects may occur, which increases non-radiative recombination pathways decreasing $V_{oc}$ and $J_{sc}$ and hence PCE.

### 4.7.2 Absorption Energy Calculations for R-III-P+m and S-P+m

To better quantify the stabilization of these systems, the adsorption energy was calculated using Eq. (15). While the absolute energy changes are known, the reaction path may require a higher activation energy than the differences indicated below. The adsorption energies for each of these systems have been tabulated in table 6.

In table 6, $E^*$ and $E^\circ$ are only shown for the slab as the calculation when the slab and monolayer are artificially separated have the same simulation set-up as each other. With the monolayer, the k-points change and the volume of the simulation cell changes, and are not comparable. With the above values, it is evident that the
Table 6: Absorption energies and related values for the investigated lead terminated slabs. The ‘energy’ values for the modified slab (A+B), slab, and monolayer are shown for demonstration of the calculation.

<table>
<thead>
<tr>
<th></th>
<th>R-III-P+m</th>
<th>A+B</th>
<th>Monolayer</th>
<th>Slab</th>
<th>Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^\circ$(eV)</td>
<td>-390.754</td>
<td>-64.300</td>
<td>-325.521</td>
<td>-325.450</td>
<td>-0.932</td>
</tr>
<tr>
<td>$E^*$ (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^*_{g,s}$</td>
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<table>
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<th>S-P+m</th>
<th>A+B</th>
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<th>Slab</th>
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<tbody>
<tr>
<td>$E^\circ$(eV)</td>
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<td>-64.300</td>
<td>-324.128</td>
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<td>-0.686</td>
</tr>
<tr>
<td>$E^*$ (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^*_{g,s}$</td>
<td>0.043</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Energy changes significantly from adsorption of the monolayer. Also, the adsorption in which m binds in a planar position adsorbs ~ 300 meV stronger to the perovskite surface. This infers better charge transfer at the interface in R-III-P compared to S-P [39].

4.7.3 Charge Density Analysis of R-III-P+m and S-P+m

To better understand how these energy differences may manifest at the interface, the charge density difference plots are examined to observe charge redistribution. The charge density difference plots are generated by artificially separating the monolayer and slab, freezing the atoms in their positions, and running a static calculation, and plotted via Eq. (16). In these charge density difference plots, yellow regions indicate electron accumulation, and blue regions are areas of charge depletion.

In Fig. 24, the charge density difference plots for R-III-P+m is shown. There are apparent redistribution of charges for R-III-P+m where the delocalized $\pi$-electrons in the benzene ring are depleted over the surface of the perovskite and aggregate towards sulfur. This may act to bond with aromatic organic HTMs via $\pi-\pi$ interactions as seen in carbazole SAMs [2]. As previously stated, C$_6$F$_5$SH initially provided longevity in humid climates compared to untreated MAPbI$_3$ cells [10], and there may
be a similar effect by reorganization of electron density. Moreover, electron density is pulled away the sulphydryl hydrogen, and potential bond formation of Pb-S via redistribution of electron density. Movement of the charges local to the -SH moiety may imply weak hydrogen bonding to the local iodine, as seen more clearly in the alternate orientation of Fig. 32(a) where electronic density are donated from iodine to attain a weak $\delta^-_I \cdots \delta^+_{H}$ interaction. Notably, at this isosurface there is no significant impact on the underlying MA$^+$ even in the closest layer to the surface. These reorganization of electronic charges induce an electric dipole at the interface, potentially modulating the band structure and charge carrier dynamics [20]. Due to the change of bonding mechanism, the charge density difference plot for S-P$+m$ appears differently, as shown in Fig. 25.

In S-P$+m$, there are redistribution of charges within the monolayer, and the same pull of electronic density results near the -SH moiety. Interesting behavior
Figure 25: Charge density plots for S-P+m magnified at the interface drawn at 0.00075 e/bohr$^3$ isosurface values a) in standard crystallographic orientation b) magnified at the interface to better show charge redistribution

manifests here as the hydrogen weakly interacts with two of the surface iodines, and there is no apparent bonding with lead. This is unexpected as sulfur is expected to bond with Pb via hard-soft acid base theory [34] and experimental results from Lu et al. [31]. Since there is much less charge redistribution at the surface, the resultant lower magnitude of the adsorption energy for S-P+m compared to R-III-P+m is reasonable. This supports the parallel versus perpendicular orientation allowing for lower lattice mismatch, which in general increases solar cell efficiency, assuming all other factors are equal [48] [21]. Additional benefit of having a parallel orientation to the surface is an increase in the dipole strength at the interface, which helps drive charge separation and reduces interfacial recombination [12] [39].
4.7.4 Average Local Potential Plots for R-III-P+m and S-P+m

The average local potential yields insight for charge transfer processes, potential differences, and generates an easily interpretable result. As shown in Fig. 26, the average potential at the monolayer sits considerably higher than the PbI layer in both cases, and thus electrons would be less likely to flow from the perovskite into the monolayer, effectively passivating the trap states at the interface [12]. For the case of S-P+m, where throughout the slab the orientation of the MA+’s varies through the stack and the flexible structure of the PbI framework is more apparent. The local potential reflects this and the periodicity is less apparent, and this is a direct result of the dipole alignment. In the case of R-III-P+m, the regularity of the structure, and counteracting dipoles in the layers allows for easier view of the periodicity. It is also possible to note here that the local potential for the MAI layers rest at higher potentials than the PbI layers. Due to the local potential driving electrons into the perovskite, and away from the monolayer, charge separation is preferred and hence solar cell performance should increase to reflect this. In other words, the resultantly more positive local potential should encourage electrons to move away from C₆F₅SH and towards the ETM decreasing interfacial recombination. Additionally from Fig. 26, the overall average of the electrostatic potential of S-P+m is slightly more positive, and thus the R-III-P+m structure may warrant better PCE due to an on average larger voltage drop across the [HTM+m]—Perovskite interface in the Debye layers [18].
Figure 26: Top structure: Charge density difference plot for \textbf{R-III-P+m}. Top graph: Planar average of the local potential along the \textit{c} direction for \textbf{R-III-P+m}. Bottom graph: Planar average of the local potential along the \textit{c} direction for \textbf{S-P+m}. Bottom structure: Charge density difference plot for \textbf{S-P+m}. Structure unit cells are aligned with their respective graphs.
4.7.5 Total and Projected Density of States for R-III-P+m and S-P+m

To further investigate the impact of the monolayer adsorption, the Density of States (DOS) were calculated for the modified slabs, as well as the pristine slab - the relaxed slab prior to monolayer absorption. In Fig. 27, the total density of states near the Fermi energy for the lead terminated slabs are shown.

![Figure 27: Total density of states magnified near the Fermi Energy for the pristine slabs R-III-P and S-P, and surface modified R-III-P+m and S-P+m. Each of these have been fermi shifted such that E(0)=E_{Fermi}](image)

Here there is a dramatic difference between the two slabs and their modified counterparts - the S-P and S-P+m structures yield a dramatically reduced bandgap roughly 0.5 eV, while the R-III-P and R-III-P+m show much more semiconductor-like behavior. The bandgap for the R-III-P and R-III-P+m are found to be 1.6719 eV and 1.760 eV respectively as calculated by occupancies at the Γ-point compared to experimentally reported values of bulk MAPbI₃, ∼ 1.6 − 1.7eV [2] [21], and is similar to what is shown in other DFT works [17] [33]. Upon surface modification, the band gap increases due to shift of the Conduction Band Minimum (CBM) in the R-III-P+m structures. It is noted that for a totally accurate calculation of the
band gap, inclusion of spin-orbit coupling or other refinements may be required due to Rashba splitting [4] or other relativistic effects due, especially to lead.

The difference exhibited in the $S-P+m$ and $S-P$ DOS from the bulk structure (reported in section 4.3) is attributed to a few possible causes. The first of these is the intrinsic difference between an effectively 2-dimensional slab and a 3-dimensional bulk. When integrating over $k$-space for the bulk, the dimensions of the BZ were defined by the mesh of $3 \times 3 \times 2$ $k$-points, while for the slabs, the BZ was defined by the mesh of $3 \times 3 \times 1$. This has the effect of losing a dimension of periodicity in the slab and modified slab configurations, which causes additional variation (fluctuations) in the DOS of the bulk structures explaining the spiky appearance for the bulk DOS versus the smoother DOS of the slabs. Additionally, the existence of surface states, those which are not present in the bulk, are capable of manifesting at the surface and back of the slab. When these states, combined with the aligned dipoles of the MA+ ions, are present, severe shifting of the conduction and valence bands is observed.

To investigate the nature of the states near the fermi energy, we examine the projected density of states for each of the elements. Use of this can indicate the elements which construct the VBM and CBM, and comparison of the surface modified slabs to their pristine variant enables one to view hybridization of states due to bonding. These can be seen in Fig. 28. As expected, due to the large quantity of iodine and lead and their number of electrons, they are the most prevalent in the density of states.
As depicted in Fig. 28, for **R-III-P** there is little modification of the density of states of iodine, where in the pristine and modified slab, manifests as a single peak at $-1.5\text{eV}$. It is also possible to observe the HOMO of the monolayer, which is close to with the VBM of the perovskite. In solar cells, the proximity of the HOMO to VBM typically increases the open circuit voltage [2], as seen in PTAA and Spiro-OMeTAD [46]. Additionally, we infer that the valence band and conduction bands remain unaltered, seeing that the I states dominate in the valence band and Pb states...
are dominant in the conduction band.

For S-P, however, there is little modification of the density of states of iodine, where in the pristine and modified slab manifests as a broad quintet centered at $-2.5$ eV. In comparison to the R-III-P+m, lead states are shifted from the conduction band towards the valence band. The states of sulfur also appear closer to the fermi level, shifting an eV from R-III-P+m to S-P+m. This implies that the orientation of the methylammonium ions and hence the dipole arrangement can greatly impact the band structure and electronic properties when aligned in a single direction, as the \textbf{R} family of structures do not possess this result. To further examine these differences in the Pb and I states, $lm$-decomposed density of states shows the orbital contribution for lead and iodine near the fermi energy.

As depicted in Fig. 29, we examine that the band gap in \textbf{R-III-P} and \textbf{R-III-P+m} is dominated mostly by I(5p)$\rightarrow$Pb(6p). This is in line with ultraviolet photoelectron spectroscopy done by Umebayashi et al. \cite{58}, where they state the main components of the valence band are the I 5p orbitals and the conduction band is dominated by the Pb 6p and I 5p orbitals which is depicted in the top half of the graph. In the \textbf{S} arrangement, lowering of the Pb\textsubscript{p} character in the CBM towards the VBM would imply hybridization, but it is shown that very weak modulation of the surface charges occur. Thus, the modification of the DOS is due to surface states that arise from the lack of periodicity to stabilize the dipoles of MA within the perovskite, and in this particular case, dramatically changes the electronic structure of the slab.

4.8 Energetics and inferences for MAI Terminated Slabs

This subsection is dedicated to specifically the geometry of monolayer adsorption, charge density analysis, local potential analysis and comparison of density of states for the MAI terminated slabs.
Figure 29: $lm$-decomposed projected density of states for: (top left) R-III-P+m, (top right) pristine R-III-P, (bottom left) S-P+m, (bottom right) pristine S-P

4.8.1 Geometry of Monolayer Absorption in MAI Terminated MAPbI$_3$

As depicted in Fig. 30, there is significant change in the monolayer position, but little change in the overall appearance of the slab and monolayer. The initial distance between the sulfur of C$_6$F$_5$SH and the iodines of the slab was set at a distance of 3.06Å, as specified in Eq. (14). The distance between neighboring methyl groups was also equivalent, but outside of expected interaction. This resulted in the monolayer being placed 1.5Å over the center of the center of the iodines ($z_{max,I}$) which increased after...
relaxation. The movement is almost exclusively 1.15 Å in the c direction with roughly 0.2 Å shifts in the [110] direction as well. This increases the distance from the iodine atoms asymmetrically to 4.02 Å and 3.65 Å. Though the C₁-S bond rotates by 70°, the S-H···I angle is preserved at 108.2° but the H···I distance increases from 2.35 Å to 2.99 Å upon relaxation.

Figure 30: Monolayer-modified R-II-M+m a) Initial positions b) Magnified view highlighting the difference in positions where the initial positions are greyed out, and the final positions are colorized.

This shows little interaction or bonding with the perovskite slab, and the PbI₆ framework remains mostly stationary. With the orientation of the MA⁺ in the structure S-M, comparatively more intense interaction occurs as shown in Fig. 31.

The adsorption mechanism for S-M+m is a bit different, where little reorientation and movement of the monolayer occurs and secondary bonding dominates. Most remarkable is the reorientation of the cations, rotating outwards by 25.7° and 29.8°. The distance between neighboring methyl groups were equivalent, but slightly outside of expected interaction distances by Eq. (14) (∼ 2.91 Å compared to ideal ∼ 2.70 Å),
and the distance between neighboring iodines were asymmetric, 4.09Å and 3.140Å. This asymmetry is required when the distance between neighboring atoms is too large, see Appendix for details. This resulted in the monolayer being placed 0.2Å from the slab surface, 3.09Å over the iodine bridging the lead atoms in the next layer down. After optimization, the monolayer moves upward in the c direction by 0.400Å and rotates 3° about the b-axis. The C₁-S bond rotates 49.75°, changing the C₂-C₁-S-H dihedral angle from 91.65° to 141.40°. This orients the sulfhydral group towards the proximal surface iodine, increasing the S-H···I bond angle from 130.1° to 164.05° and decreasing the H···I length from 3.088Å to 2.559Å. Visually, the location of the monolayer yields some distortion in the lattice, potentially introducing some lattice mismatch, but of the considered orientations it was found to be thermodynamically most stable.
4.8.2 Absorption Energy Calculations for R-II-M+m and S-M+m

To better quantify the stabilization of these systems, the adsorption energy is calculated as Eq. (15). The adsorption energies for each of these systems and their differences have been tabulated in Table 7.

Table 7: Absorption energies and related values for the investigated MAI terminated slabs. A+B indicates the modified slab, and the relative ‘energies’ are shown for calculation purposes.

<table>
<thead>
<tr>
<th>R-II-M+m</th>
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<th>Monolayer</th>
<th>Slab</th>
<th>Adsorption</th>
</tr>
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</tr>
<tr>
<td>$E^\ast (eV)$</td>
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<td>-326.161</td>
<td>-326.161</td>
<td>-0.399</td>
</tr>
<tr>
<td>$E^\ast_s-E^\circ_s,g$</td>
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<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>S-M+m</th>
<th>A+B</th>
<th>Monolayer</th>
<th>Slab</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$E^\circ (eV)$</td>
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<td>-325.663</td>
<td>-0.622</td>
</tr>
<tr>
<td>$E^\ast (eV)$</td>
<td>-393.726</td>
<td>-325.804</td>
<td>-325.663</td>
<td>-0.622</td>
</tr>
<tr>
<td>$E^\ast_s-E^\circ_s,g$</td>
<td>0.141</td>
<td>0.141</td>
<td>0.141</td>
<td>0.141</td>
</tr>
</tbody>
</table>

Contrasting the behavior of the lead terminated slabs, the MAI terminated slab binds much more strongly to the perovskite, a difference of 223 meV from S-M+m to R-II-M+m, which may imply that the interaction and hence interfacial recombination may be more optimal for S-M+m. However is observed that there is a relatively significant deformation of the perovskite occurs for the S-M+m case, increasing in energy from the ground state by 141 meV. The opposite behavior is observed for the R-II-M+m frustrated slab, where there is practically no difference in the perovskite energy and thus may discourage the formation of defects. It is also useful to then compare the absorption energy differences for the PbI and MAI terminated slabs. As seen in the previous section, the adsorption energies for PbI terminated slabs were much larger in magnitude, with R-III-P+m and S-P+m having $E_{Ads}$ of $-0.932$ and $-0.686$ eV respectively. This likely results from the MAI terminated slabs being relatively stable on their own. For the PbI terminated slabs, a missing iodine atop the Pb atoms induces additional energy, readily attempting to stabilize the charge
via interaction with the sulphydryl group.

4.8.3 Charge Density Analysis of \textbf{R-II-M+m} and \textbf{S-M+m}

To better understand how these energy differences may manifest at the interface, the charge density difference plots are examined to observe charge redistribution. In these charge density difference plots, blue regions indicate negative values, or accumulation of electrons (charge accumulation) and yellow regions are areas of charge depletion.

![Charge density plots for \textbf{R-II-M+m} magnified at the interface drawn at 0.00075 eV/Bohr$^3$ isosurface values a) in standard crystallographic orientation b) magnified at the interface to better show charge redistribution.]

Figure 32: Charge density plots for \textbf{R-II-M+m} magnified at the interface drawn at 0.00075 eV/Bohr$^3$ isosurface values a) in standard crystallographic orientation b) magnified at the interface to better show charge redistribution.

In Fig. 32, the charge density difference plots for \textbf{R-II-M+m} is shown. Here, iodine and hydrogen clearly show interaction, forming hydrogen bonds via $\delta_H^+ \cdots \delta_I^-$. This is assisted by withdrawal of electrons towards sulfur which then weakly interacts with the surface MA group. Due to the lack of prominent dipoles on the surface charge separation may not be as prominent as the previous investigated slab structures [20].
Due to the change of bonding mechanism, the charge density difference plot for $S$-$M+m$ appears differently, as shown in Fig. 33.

![Charge density plots](image)

Figure 33: Charge density plots for $S$-$M+m$ magnified at the interface drawn at 0.00075 eV/Bohr$^3$ isosurface values a) in standard crystallographic orientation b) magnified at the interface to better show charge redistribution.

In $S$-$M+m$, there are redistribution of charges within the monolayer, and the same pull of electronic density results near the -SH moiety. Here though, there are much larger areas that are impacted. Hydrogen bonding is observed in this system via $\delta^+_{H} \cdots \delta^-_I$ and more of the electronic density from the aromatic section is accessed. This movement of electronic density out of the aromatic pentafluorobenzene is expected to modulate the HOMO and LUMO of the monolayer [57]. Since there is much more charge redistribution at the surface, the resultantly higher magnitude of the adsorption energy for $S$-$M+m$ compared to $R$-$II$-$M+m$ is reasonable. Additional benefit is an increase in the dipole strength at the interface - which helps drive charge separation and reduces interfacial recombination [12] [39].
4.8.4 Average Local Potential Plots for R-II-M+m and S-M+m

From these results, to understand the charge transfer mechanism at the interface and infer the impact on charge carriers, the average local potential in the c direction is shown in Fig. 34 for both of the modified MAI terminated slabs. As shown in Fig. 34, the average potential at the monolayer sits considerably higher than the PbI layer in both cases, and thus electrons would be less likely to flow from the perovskite into the monolayer, effectively passivating the trap states at the interface [12]. However, it is noted that for the PbI terminated slabs, the barrier is much higher which would better passivate the interface. For the case of S-M+m, where throughout the slab the orientation of the MA+’s are aligned in the c direction through the stack, the impact of the aligned dipoles is once again present. This is exhibited by a beat-like pattern in the local potential of the S family of the slabs, while the opposing dipoles in the layers equilibrate this effect. In the case of R-II-M+m, the regularity of the structure allows for easier view of the periodicity throughout layers. As noted in previous sections, the orientation of the MA ions in the R-II-M+m structure flip at the top of the perovskite. This effect on the planar average potential is not very pronounced in this data; the peak corresponding to the seventh layer (terminal PbI), drops slightly, but this is also observed in the S-M+m data. It is also possible to note here that the average local potential for the MAI layers rests at higher potentials than the PbI layers. Due to the local potential driving electrons into the perovskite and away from the monolayer, charge separation is preferred and hence solar cell performance should increase to reflect this. Additionally from Fig. 34, the planar average of the electrostatic potential of S-M+m is slightly more negative at the perovskite side of the interface, and thus the S-M+m structure may warrant better PCE due to an on average larger voltage drop across the [HTM+m]—Perovskite interface in the Debye layers [18].
Figure 34: Top structure: Charge density difference plot for R-II-M+m. Top graph: Planar average of the local potential along the c direction for R-II-M+m. Bottom graph: Planar average of the local potential along the c direction for S-M+m. Bottom structure: Charge density difference plot for S-M+m. Structure unit cells are aligned with their respective graphs.
4.8.5 Total and Projected Density of States for R-II-M+m and S-M+m

To further investigate the impact of monolayer adsorption, the density of states were calculated for the modified slabs, as well as the pristine slab - the relaxed slab prior to monolayer adsorption. In Fig. 35, the partial density of states for each element are shown.

![Graph showing density of states](image)

Figure 35: Total density of states magnified near the Fermi Energy for the pristine slabs R-II-M and S-M, and surface modified R-II-M+m and S-M+m. Each of these have been fermi shifted such that $E(0) = E_{Fermi}$.

As with the lead terminated slabs, there is a noteworthy difference between the two slabs and their modified counterparts. The S-M and S-M+m structures yield a dramatically reduced bandgap of roughly 0.4 eV. The band gap for the R-II-M and R-II-M+m are found to be 1.725 eV and 1.705 eV respectively as calculated by occupancies at the Γ-point compared to experimentally reported values of bulk MAPbI$_3$, $\sim 1.6 \text{ }-\text{ } 1.7$ eV [2] [21], and is similar to what is shown in other DFT works [17] [33] and compares well to the lead terminated R-III-P slabs. Upon surface modification, the band gap decreases due to shift of the CBM in the R-II-M+m structures. The difference exhibited in the S-M+m and S-M DOS compared to the
R-II-M(+m) is similar to that seen in the last section, section 4.7.5. The differences seen in these DOS plots are ascribed to occur via the same mechanisms, manifesting most directly from the dipoles for MA aligning and modifying the surface states.

![DOS plots](image)

**Figure 36:** Projected density of states separated by elemental contribution for: (top left) R-II-M+m, (top right) pristine R-II-M, (bottom left) S-M+m, (bottom right) pristine S-M

The projected density of states for each of the elements was then examined. This can indicate the elements which construct the VBM and CBM, enables one to view hybridization of states due to bonding when comparing the pristine and modified architectures. These can be seen in Fig. 36. These results also mirror those obtained...
for R-III-P(+m) and S-P(+m). Within R-II-M there is little modification of the density of states of iodine, where in the pristine and modified slab, manifests as a single peak at $-1.5 \text{ eV}$. However, when modified, there are an increase of states is available near $E_{\text{fermi}}$. It is also possible to observe the HOMO of the monolayer, which is close to with the large concentration of Pb and I states of the perovskite which typically increases the $V_{\text{ac}} [2]$, as organic HTMs [46]. Additionally, we infer that the valence band and conduction bands remain unaltered, seeing that the I states dominates the valence band and Pb states dominate the conduction band.

For S-M, however, there is little modification of the density of states of lead, but the iodine states are comparable to S-P. This alteration of the states arises from the capping layer of PbI in S-P, and free motion of MA in S-M. Comparing S-M to R-II-M+m, lead states are shifted from the conduction band towards the valence band. The states of sulfur also appear closer to the fermi level, shifting an eV from R-III-P+m to S-P+m. This implies that the orientation of the methylammonium ions and hence the dipole arrangement can greatly impact the band structure and electronic properties when aligned in a single direction, as the R family of structures do not possess this result. To further examine these differences in the Pb and I states, $lm$-decomposed density of states shows the orbital contribution for lead and iodine near the fermi energy.

As depicted in Fig. 37, we examine that the band gap in R-II-M and R-II-M+m is dominated mostly by $I(5p)\rightarrow \text{Pb}(6p)$. This is in line with results from the previous section and experimental findings [58]. The story for S-M and S-M+m resembles results garnered from S-P and S-P+m. In the S arrangement, lowering of the Pb$_p$ character in the CBM towards the VBM would imply hybridization, but it is shown that very weak electronic modulation of the pristine surface occurs, and the deformation on the surface may incur a slight change in the appearance of the I(5p) states. Thus, the modification of the DOS is due to surface states that arise from the
lack of periodicity to stabilize the dipoles of MA within the perovskite, and in this particular case, dramatically changes the electronic structure of the slab.

4.9 Theoretical Solar Cell Efficiencies

Finally, the detailed balance limit is used again to compare the theoretical maximum solar cell performance of the bulk structures, slabs, and the modified slabs. These are tabulated in table 8. Obviously the reported values above are higher than
Table 8: Values for the bandgap and theoretical maximum solar cell performance of each of the bulk and slab structures using the detailed balance limit as suggested by Rühle [47]. These operating conditions assume AM 1.5G illumination and an operating temperature of 25°C.

<table>
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<th>$J_{mpp}$ (mA cm$^{-2}$)</th>
<th>$V_{mpp}$ (V)</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>†S</td>
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<td>1.604</td>
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</tr>
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<td>1.604</td>
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</tr>
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<tr>
<td>†R-I-M</td>
<td>1.626</td>
<td>24.31</td>
<td>1.227</td>
<td>29.82</td>
</tr>
<tr>
<td>R-II-M</td>
<td>1.725</td>
<td>21.50</td>
<td>1.319</td>
<td>28.35</td>
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<tr>
<td>R-III-M</td>
<td>1.698</td>
<td>22.02</td>
<td>1.301</td>
<td>28.64</td>
</tr>
<tr>
<td>R-IV-M</td>
<td>1.681</td>
<td>22.61</td>
<td>1.283</td>
<td>28.98</td>
</tr>
<tr>
<td>S-P</td>
<td>$\sim$ 0.5</td>
<td>60.08</td>
<td>0.232</td>
<td>13.94</td>
</tr>
<tr>
<td>R-I-P</td>
<td>1.667</td>
<td>22.92</td>
<td>1.273</td>
<td>29.17</td>
</tr>
<tr>
<td>†R-II-P</td>
<td>1.650</td>
<td>23.57</td>
<td>1.255</td>
<td>29.57</td>
</tr>
<tr>
<td>R-III-P</td>
<td>1.672</td>
<td>22.92</td>
<td>1.273</td>
<td>29.17</td>
</tr>
<tr>
<td>R-IV-P</td>
<td>1.665</td>
<td>22.92</td>
<td>1.273</td>
<td>29.17</td>
</tr>
<tr>
<td>R-III-P+m</td>
<td>1.760</td>
<td>20.37</td>
<td>1.356</td>
<td>27.62</td>
</tr>
<tr>
<td>S-P+m</td>
<td>$\sim$ 0.4</td>
<td>57.29</td>
<td>0.152</td>
<td>8.73</td>
</tr>
<tr>
<td>†R-II-M+m</td>
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<td>22.02</td>
<td>1.301</td>
<td>28.64</td>
</tr>
<tr>
<td>S-M+m</td>
<td>$\sim$ 0.5</td>
<td>60.08</td>
<td>0.232</td>
<td>13.94</td>
</tr>
<tr>
<td>††Son et al. [53]</td>
<td>1.6</td>
<td>23.40</td>
<td>1.118</td>
<td>19.8 ± 0.63</td>
</tr>
</tbody>
</table>

†- Indicates highest theoretical PCE for category.
‡- Indicates experimental result.

those found in literature for a single junction device with that given bandgap, though there is great interest in developing devices that exceed the Shockley-Quessier (SQ) or detailed balance limit, however that is beyond the scope of this work. To show this, a very high performing pure MAPbI$_3$ solar cell as generated by Son et al. [53] has been included. This reduction from the maximum values is due to recombination pathways, and non-optimal absorption. For recombination pathways, dipoles that are present at the interfaces can help mitigate this to enhance charge separation. As for non-optimal absorption, the SQ assumption of a step function is impractical in
reality, though, access to upper excited states may reduce this problem. Moreover, dislocations and defects in the crystal structure increase the mechanisms for which carriers can recombine but the long carrier lifetimes in these materials make this less of an issue [21].

Table 8 aids in showing the impact of decrease in $E_g$, and the impact on the optimal $J_{mpp}$ and $V_{mpp}$. Clearly, when the band gap decreases, as seen with the S slabs, the current density increases dramatically. This results from the increase in the number of photons which are capable of exciting to the conduction band in the SQ assumption, all photons of $E \geq E_g$ create an electron-hole pair. Now, due to the amount of thermal relaxation that must occur from the high energy photons, as well as the small bandgap, the voltage generated must be very low. This has a dramatic effect on the solar cell performance, reducing the optimal PCE from nearly 30%, to at its lowest $\sim 8\%$.

This drastic reduction in theoretical PCE may help or hinder the device function. An overall increase in the number of charge carriers may drive a greater current through the device, or these states could recombine and annihilate diminishing performance. This effect may be rather insignificant, as the surface states comprise a very small portion of the available bulk states in a fully crystalline material. In the event that surfaces may be present, which would be the result of grain boundaries or other defects present in the bulk material, surface-like behavior may manifest. As a result, granular solar cells may exhibit slightly lower band-gaps compared to their single-crystal counterparts, but these effects due to defects and inhomogeneities are not part of this work. However, it has also been noted that for these devices, there are generally large loses at the perovskite—HTM layer, which may be the result of poor energetic alignment or other losses at the interface [9] [46]. Since these great changes to the states of the system only occurred during alignment of the methylammonium ions, an energetically unfavorable configuration for the slab surface, it is suggested
that this state may be less active in devices with no electric field being applied. When a sufficient electric field is applied, the alignment of the MA$^+$ along the direction of the electric field is probable [29]. As shown in the previous results, global alignment of MA$^+$ has a significant impact on the density of states, energy gap, stability, and solar cell performance of hybrid perovskite solar cells. Through the careful balancing of dipoles within the MAPbI$_3$ architecture, the surface states can be well arranged and act like the bulk structure, resulting in greater performance and stability.
5 Conclusion

This work presents the idea that adsorption energetics of pentafluorobenzenethiol may be modified by the orientation of methylammonium ions with MAPbI$_3$ using $ab\ initio$ calculations. Additionally, it shows that the DOS and electronic structure of MAPbI$_3$ can be greatly modified by the presence of surface states, and orientation of MA$^+$. When each of the methyammonium ions were aligned in the $c$ direction, the resulting surface charges on either side of the perovskite destabilizes the surface states. However, the surface states comprise a significantly small part of the total states in an actual material, and thus the resulting effect on a working device may have a diminutive impact on performance.

Additionally, the relative energy differences in multiple structures including bulk structures and PbI and MAI terminated slabs are reported, indicating the stable geometries where the MA$^+$ are oriented in parallel alignments. This provides more opportunities to study the effect of non-parallel orientations using a high throughput method to attempt to measure the effect of MA$^+$ dipoles on the electronic structure or PCE. More extensions could be to examine, using molecular dynamics, the energetic barriers for reorienting in each of these directions. This would provide reasoning about how active each of these rotational modes may be at room temperature or higher operating temperatures. These insights may parallel to other perovskites materials used for solar cells i.e. those which are lead-free.

We are also capable of showing changes in the most stable geometries of thiol adsorption are modulated by the global orientation of methylammonium cations. It is also suggested, with the results of charge density difference plots, that strong dipoles are induced when the monolayer is parallel to the surface, which may support future
monolayer developments. While it was not observed, monolayers that provide a sufficiently large electric field at the interface may force rearrangement of the MA\(^+\) near the interface, which would also modulate the performance of these devices. To conclude, we demonstrate the reasons that methylammonium orientation impacts thermodynamically stable configurations and the resultant stereochemical implication of adsorption on MAPbI\(_3\) surfaces, and provide theoretical discussion on corresponding solar cell performance.
6 Appendix

6.1 PDOS of R-II, R-III, R-IV

The elemental PDOS and \( lm \)-decomposed PDOS for Pb and I for R-II are shown in Fig. 38. For R-II calculating the bandgap for this system by taking the closest direct gap at any \( \mathbf{k} \)-point is 2.033 eV (at the \( \Gamma \)-point). Comparing this value to Rühle's table of values, the optimal \( J_{mpp} \) is 13.71 mA/cm\(^2\), \( V_{mpp} \) is 1.604V, and the maximum PCE is 21.98%. The related plots for R-III are shown in Fig. 39.

For R-III calculating the bandgap for this system by taking the closest direct gap at any \( \mathbf{k} \)-point is 2.034 eV (at the \( \Gamma \)-point). Comparing this value to Rühle's table of values, the optimal \( J_{mpp} \) is 13.71 mA/cm\(^2\), \( V_{mpp} \) is 1.604V, and the maximum PCE is 21.98%. The related plots for R-IV are shown in Fig. 40.
Figure 39: (Left) Elemental Projected Density of States and (Right) $lm$-decomposed PDOS for bulk R-III.
For R-IV, calculating the bandgap for this system by taking the closest direct gap at any \( k \)-point is 2.003 eV (at the \( \Gamma \)-point). Comparing this value to Rühle’s table of values, the optimal \( J_{mpp} \) is 14.35 mA cm\(^{-2}\), \( V_{mpp} \) is 1.577 V, and the maximum PCE is 22.62%. These results have been tabulated in table 3.

### 6.2 Solutions to the Bonding Equation

Due to the sparsity of the atoms on the surface, some of the ideal bonding lengths that we chose to use, for fairness of chemisorption and physisorption, were not capable of satisfying all constraints. For locations over a single point, it is trivial. When the distance needs to be balanced between 3-4 points, the solution becomes more challenging. This is overcome by minimization of a cost function, and algorithmically solving it as an optimization problem. For the equation:

\[
d_m \approx \frac{1}{2}(r_{vdw}^S + r_{vdw}^j + d_{cov}^{S-j}) \forall j_b
\]

subject to \( z_S \geq z_{slab} \)
The cost function is generated via:

\[
f(\theta) = \sum_{j_{\text{bonding}}} (|r_j - p| - d_{j_{\text{bonding}}})^2 \forall j_{\text{bonding}}
\]  

(27)

Where \( p \) is the coordinates of the solution, and vertical bars are the norm operation. For the central positions, effort is made to satisfy the top most I, Pb, C, and N atoms. When large costs arose, elements were removed one by one to assess the cost, and the process repeated until a sufficiently small cost resulted.
References


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