Hybrid organic-inorganic perovskites (HOIPs) have emerged to the forefront of optoelectronic materials advancement in the past few years. Due to the nature of organic compounds within the perovskite structure, its optoelectronic properties are affected by complex interaction and correlation effects between the organic and inorganic ions. Using spectroscopic ellipsometry, we observe two broad plasmonic excitation from the calculated
loss function (LF), \(-\text{Im}[\epsilon^{-1}(\omega)]\), peak A’ and B’ at 3.28 eV and 4.26 eV, respectively. The presence of these two asymmetric peaks in the spectroscopic ellipsometry (SE) spectra indicates the existence of unconventional plasmons at room temperature. This is inferred due to the absence of the zero-crossing in the real part of dielectric function \(\epsilon_1(\omega)\). Through combined Near-Edge X-ray Absorption Fine Structure (NEXAFS) and Resonant Photoemission Spectroscopies (ResPES), we observe resonance enhancement peak close to 15 eV in the C K-edge region that unravels a charge transfer event due to the opening of an extra autoionization channel. Additionally, photoluminescence (PL) spectrum confirms the presence of broadband emission originating from the self-trapped emission excitons at 2.38 eV due to the soft 2D-HOIPs crystal structure. We believe that these phenomena directly impact the correlation strength in 2D-HOIPs. Our results have confirmed the existence of unconventional plasmons of 2D-HOIPs at room temperature. Such studies in the emission and plasmonic behavior of perovskites will pave the way for the efficient light emitting devices or lasers with minimal integrations of the materials.

I. INTRODUCTION

In recent years, the development of three-dimensional (3D) hybrid organic-inorganic perovskites (HOIPs) as an active material in the optoelectronic devices endowed numerous interests.\(^1\)\(^-\)\(^2\) However, long-term thermal, moisture or light-stability issue and lead toxicity are some of the issues shrouding the advancement of perovskite-based solar cells and other promising practical applications. To overcome these issues, low dimensional perovskites, spanning from 2D to 0D, offers significant enhanced thermal and mechanical stability. In addition, the replacement of lead in an effort to reduce toxicity levels ultimately push the more complex HOIPs for efficient active device configurations, exhibiting comparable performance and promising alternative to their 3D counterparts\(^3\)\(^-\)\(^5\).

Hybrid organic-inorganic perovskites, commonly in the form of \(\text{ABX}_3\), \(\text{A}_2\text{BX}_4\), and \(\text{ABB’X}_6\), where \(\text{A} = \) organic amine cations, \(\text{B} = \) Pb or other metals, \(\text{X} = \) halides, have attracted significant attention recently as they provide promising alternative to three-dimensional systems.\(^6\)\(^-\)\(^9\) In 2D HOIPs structures, the inorganic components, consisting of \(\text{BX}_4\) elements, are oriented along (001)-terminated perovskite sheets and sandwiched by monovalent organic amine cations that are connected via Van der Waals forces.\(^10\) On the other end, 0D HOIPs have their inorganic octahedra isolated from any particular structure, only surrounded by the organic cations\(^11\). Interestingly, these layered perovskite structure tend to be more resistant against humidity.\(^12\)\(^-\)\(^13\) Due to its diverse candidates and chemically abundance in nature, HOIPs demonstrate versatile structural flexibility, diversity, and outstanding optoelectronic performance, giving rise to various applications in devices such as solar cells\(^14\)\(^,\)\(^15\), field-effect transistors\(^16\), photodetectors\(^17\), lasing\(^18\)\(^,\)\(^19\) and light-emitting devices\(^9\)\(^,\)\(^20\).
The highly diverse applications of HOIPs is largely attributed to its dramatic change in their physical and chemical properties when A-, B-, or X-sites are substituted. A chemical substitution in a specific site will induce changes such as: 1) A-site substitution typically does not directly affect the inorganic perovskite electronic structure, but this factor play a role in the dimensionality of the perovskite\textsuperscript{6-11}; 2) X-site substitution dictates the valence band energy that commonly alters the observed electronic band gap\textsuperscript{21}, and ; 3) B-site substitution controls electronic structure and the optoelectronic properties by changing the conduction band and as a result modify the electronic states around the Fermi level.\textsuperscript{22} Furthermore, HOIPs also exhibit broadband PL emission and self-trapped excitons (STEs), which is highly dependent on the chemical composition and “soft” crystal structure\textsuperscript{7,8}. These effects are highly complex and oftimes difficult to determine its origins\textsuperscript{23}. It proves that the addition of organic components is directly impacting the electron interactions and correlation effects in HOIPs and requires more extensive study on the origins of such behaviors.

Meanwhile, fully inorganic perovskites and oxides are equally complex in terms of electronic structure and their correlation effects, where some aspects related to mott-insulators and frustrated magnets exhibited complex phenomena such as anomalous excitons, room temperature ferromagnetism, and metal-insulator transitions\textsuperscript{24-26}. In fact, due to the strong electron correlations, inorganic materials such as SrNbO\textsubscript{1+x} and Eu\textsubscript{0.3}Ba\textsubscript{0.7}Ti\textsubscript{1-x}Nb\textsubscript{x}O\textsubscript{3} are reported to exhibit a newly discovered type of plasmons. These plasmons are quasi-local in nature with multiple plasmon frequencies and low loss feature\textsuperscript{27,28}. Such plasmons exist in an insulator material possessing 2D perovskite-like crystal structure, akin to 2D HOIPs. At the same time, emission and plasmonic properties of 2D HOIPs are needed to design light emitting devices and laser within a single material\textsuperscript{29}. So far, most materials that support photonic local density of states for spontaneous emission manipulation contain separate components\textsuperscript{30}. Thus, it is of high interest to study whether the 2D HOIPs can generate such unusual plasmonic signature mediated due to strong correlations effects and explore their potential application as a single material light emitter.

In this study, we report the electronic and optical properties of lead-free 2D-layered perovskite with a homovalent replacement of Pb cations with Cu cations, or (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{2}CuCl\textsubscript{4} (hence forth referred as (MA)\textsubscript{2}CuCl\textsubscript{4}). We systematically probed the perovskite optical properties by means of Spectroscopic Ellipsometry (SE) techniques across energies range of 1.30 – 4.70 eV to extract their complex dielectric function $\varepsilon(\omega)$, reflectivity, and loss function (-Im[$\varepsilon^{-1}$]) (LF). X-ray absorption spectroscopy (XAS) and resonant photoemission
spectroscopy (RPES) reveal a charge transfer event between carbon and inorganic cations. Moreover, photoluminescence (PL) show that (MA)$_2$CuCl$_4$ exhibits broad PL emission, which is induced by the self-trapped excitons (STE). The complex charge transfer, broadband emission, and electronic correlations in the hybrid perovskites are evident in the unconventional plasmons signature, where this is manifested as the asymmetric peak line shape and a broad Full Width at Half Maximum (FWHM). We believe these new findings will spark more attempts to unravel the existence of unconventional plasmons in other HOIPs and its correlated effects on their optoelectronic properties.

II. RESULTS AND DISCUSSION

A. Crystal Structure and Morphology

We begin the discussion by exploiting the phase crystallinity and surface morphology of (MA)$_2$CuCl$_4$ using X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) as shown in Fig. 1. Previous studies on the crystal structure of (MA)$_2$CuCl$_4$ show that it forms a 2D layered structure (Fig 1a), where its symmetry was determined to be monoclinic with a P2$_1$/c space group at room temperature$^{31}$. X-ray diffraction spectrum (Fig. 1b) has confirmed that our sample is formed as a layered 2D perovskite, based on the sharp intensity of the peaks, which is directly related to the interplanar spacing of low-dimensional single crystals$^{32}$. Moreover, both AFM and SEM micrographs show a typical layered structure, with excess rounded-shaped particles likely to be excess amount of halogen precursors and a calculated surface roughness of 5.98 nm. For comparison, we also present XRD and topographic details of (MA)$_2$CdCl$_4$ and (MA)$_2$ZnCl$_4$ in Figure S1 and S2, respectively.

Due to the “soft” crystal structure of 2D hybrid perovskites, these materials exhibited diverse structural and magnetic phase transitions that are determined by their site-specific compositions$^{33, 34}$. For instance, (MA)$_2$CuCl$_4$ undergoes magnetic and structural phase transitions at two temperatures: 1) 8.9 K: Ferromagnetic anisotropy to antiferromagnetic state; and 2) 348 K: monoclinic to tetragonal symmetry$^{31, 35}$. If the transition metal is substituted, i.e. from (MA)$_2$CuCl$_4$ to (MA)$_2$CdCl$_4$, then the crystal structure undergoes two additional transitions at low temperatures$^{36}$. Furthermore, if we consider to perform halogen site substitution, i.e. (MA)$_2$CdCl$_4$ to (MA)$_2$CdBr$_4$, this would alter its dimensionality from 2D to 0D$^{37}$. In essence, the tunability of hybrid perovskites can be considered as double-edge sword, despite its wide-ranging optoelectronic properties, the underlying mechanism and their physical phenomena are still being studied$^{23, 38, 39}$. Thus, current research focuses on the
variation of specific site substitution to pinpoint the electronic and structural modifications occurring in these hybrid perovskites.

Figure 1. Crystal structure and morphology of (MA)$_2$CuCl$_4$: a) Crystal structure generated from XRD diffraction measurements and theoretical Density Function Theory calculation (DFT). The Crystal structure diagrams are generated from VESTA. b) Room temperature XRD measurements of (MA)$_2$CuCl$_4$. Micrograph feature with c) AFM tapping mode and SEM image of (MA)$_2$CuCl$_4$. Scanning size is 5 x 5 µm$^2$ with surface roughness ~ 5.98 nm.

The existence of unconventional plasmons have been found in highly correlated electron systems, where these systems include: 1) transition metals, such as Cu, Nb, and Eu; 2) Complex hybridization with O atoms; and 3) Layered inorganic crystal structures. Despite the extensively studied APbX$_3$ compounds, the latest ellipsometry measurements have shown that unusual optical transitions are also present in hybrid perovskites. However, it is likely that different physical mechanisms could govern the correlation effects in 2D HOIPs. To minimize dramatic modifications, such as dimensionality, structural, and magnetic phase transitions, we have chosen (MA)$_2$CuCl$_4$ single crystal as a model 2D hybrid perovskite to probe the existence of complex optical phenomena through spectroscopic ellipsometry technique.
B. Photoluminescence (PL) and Time-resolved Photoluminescence (TR-PL) results.

Figure 2. Steady-state photoluminescence and time-resolved PL spectra of (MA)$_2$CuCl$_4$ (a) PL spectra and absorption coefficient of (MA)$_2$CuCl$_4$. TR-PL spectra of (MA)$_2$CuCl$_4$ with emission wavelength at (b) 425 nm and (c) 520 nm, respectively. Red line indicates biexponential fitting of the raw TR-PL spectra (black).

Before we further investigated the ellipsometry properties of those 2D perovskite single crystals, we need to reconcile the fundamental optical properties of HOIPs and compared them with the existing literature$^{16,42}$. Therefore, a room temperature Photoluminescence (PL) and time-resolved Photoluminescence (TR-PL) measurements on (MA)$_2$CuCl$_4$ single crystals were carried out at room temperature (Fig. 2). In general, two characteristic PL emission peaks are expected to be observed: 1) Free exciton (FE) emission, a signature sharp peak at high photon energies, and 2) self-trapped exciton (STE) emission, a broader emission that dominating over the low energy regions$^{23,43}$. Our findings suggested that (MA)$_2$CuCl$_4$ has only broadband emission centered at 520 nm (2.38 eV) with a Stoke shift of ~1460 nm. STE emission is highly associated to the lattice deformation and the out-of-plane inter octahedral tilt angle$^{23}$. The deformed lattice would eventually mediates charge carriers to self-trapped and led to a condition of favorable energy, in turn creating a broadband emission that is similar to the intragap defect states$^{42,44,45}$. Additionally, the PL emission also depends on the out-of-plane lattice distortion,
recombination losses, and de-trapping of STE states\(^{23, 44}\). In contrast, when substituting Cu with Cd, the FE emission and STE emission peaks are visible (Figure S3). In addition, the average lifetime (\(\tau\)) of (MA)\(_2\)CuCl\(_4\) and (MA)\(_2\)CdCl\(_4\) are approximately 1 – 6 ns, which are consistent with the previous observations of STE emission\(^{42}\).

Raman technique was performed to complement the previous PL characterization in order to identify the presence of the contributing molecular groups of 2D-HOIPs as presented in Figure S4. In principle, the Raman spectrum shows three fingerprint frequency regions: a) Cu-Cl vibration modes under 350 cm\(^{-1}\) that indicates the presence of the CuCl\(_4^{2-}\) anion; b) CH\(_2\), NH\(_3\) and C-N-H vibrations modes between 350 and 1600 cm\(^{-1}\); c) C-H stretching vibrations was observed above 2500 cm\(^{-1}\). According to these vibration signatures, we confirmed the presence of 2D nature of as-synthesized (MA)\(_2\)CuCl\(_4\).

C. Near-Edge X-Ray Absorption Fine Structure and Resonant Photoemission

Figure 3. Carbon K-edge NEXAFS spectra of (MA)\(_2\)CuCl\(_4\). The angular dependent measurements were taken with grazing incidence angle 20° (black) and normal incidence 90° (red).

Next, the elucidation of the electronic structure of (MA)\(_2\)CuCl\(_4\) needs to be investigated as a platform for the ellipsometric analysis. To investigate the electronic structure in (MA)\(_2\)CuCl\(_4\), we utilized several high-resolution based synchrotron techniques such as near edge X-ray absorption spectroscopy (NEXAFS), photoemission (PES), and resonant photoemission (ResPES). By probing the core and valence electronic states through absorption and photoemission spectra, we investigate the electronic structure, possible electronic transitions and the effects of the organic ligands on the electronic structure. Moreover, the results will complement the spectroscopic ellipsometry data, as it captures the allowed dipole transitions through the unoccupied states probed by NEXAFS\(^{27}\). ResPES is intended to probe the element-specific contributions of the valence band states, thus confirming any electronic states delocalization in (MA)\(_2\)CuCl\(_4\)\(^{46}\).
We begin with the NEXAFS, where the C-K edge NEXAFS spectra of (MA)$_2$CuCl$_4$ (Fig. 3) exhibits distinctive peaks enhancements under different angle of incidence. Here, we categorize the peaks into two regimes ($\pi^*$ and $\sigma^*$ electronic transitions), where these peaks are commonly found in 283 – 290 eV energy range. The origin of the resonance peak in the NEXAFS spectrum below 285.30 eV corresponds to the $\pi^*$ resonances feature due to electronic transitions from initial states into the unoccupied (C-C) $\pi^*$ anti-bonding orbital, whereas resonant peak close to 287.8 eV is assigned to transitions involving the C atoms in the methylene units. The last two broad features around 293.3 and 300 eV are assigned to C-C ($\sigma^*$) and C-N ($\sigma^*$), respectively. When compared to the previous studies of 2D hybrid perovskites, the hybridization between halogen states (Cl 5s and Cl 5s) and methylene states (N, C 2p) can be seen in ResPES in combination with NEXAFS, which we will discuss in the following section. We observe that C 1s core level is clearly hybridized with some of the valence states and that it is highly dependent on the incidence angle. The full summary of resonance peaks identification is given in Supplementary Table S1.

Since the intensity differences are indicative of orientation linear dichroism, one should consider that the cross sectional area of the resonant photo-excitation process is highly dependent on the relative orientation of the electric-field vector ($\vec{E}$) of the incident synchrotron light with respect to the transition dipole moment (TDM) of the active material. Due to correlated transition resonance states, one could determine that the resonant excitation arises from the ground state ($1s$) to an unoccupied state where a resonant intensity is strongly sensitive to the $\vec{E}$ vector. In other words, the NEXAFS intensity is strongly enhanced when $\vec{E}$ is parallel to the governing orbital sample vector. Thus, the peak intensity become suppressed when $\vec{E}$ is perpendicular to the sample orbital vector. This is clearly shown in Fig. 3a, where we observe the transition from 1s to $\pi_1^*$ orbital at 285.3 eV, and similar behavior were reflected in the $\pi_2^*$ and $\pi_3^*$ resonant transitions. In other words, these findings qualitatively indicate that the MA moieties are lifted with respect to the lateral perovskite plane, where this consensus in many theoretical DFT calculations and experimental measurements. From the differences profile of the angle-dependent NEXAFS measurements, then the average tilt angle of MA moiety could be estimated using angular dichroism relationship based on the following equation:

$$\frac{I_{90^\circ}}{I_{20^\circ}} = \frac{1}{2} \tan^2 \theta$$

From this relationship, we estimate that the average tilt angle of (MA)$_2$CuCl$_4$ is 68.16°, which is in agreement to the finding in the calculated relaxed crystal structure of 67.7° – 69.21° (Fig. 1a). For comparison,
NEXAFS spectra of (MA)$_2$CdCl$_4$ is presented in Figure S5. Thus, interaction between the organic molecules and the transition metal is significantly impacts the orientation of the organic moiety and how they interact with the inorganic components. We will investigate this effect in PES and ResPES discussion in the following section.

To indicate any chemical interaction between the MA moieties and the inorganic elements, we sweeping the core level of carbon 1s to assess the sample chemical compositions. Figure S6a shows that the evolution of C 1s core level state is centered at 286.60 eV. This prominent peak is typically found in most of HOIPs originating from the C-N bonding signature. To substantiate the finding, the N 1s core level at 402.60 eV and Cl 2p also display the expected respective signals at and 2p$_{3/2}$ = 198.5 eV; 2p$_{1/2}$ = 200.1 eV as shown in Figure S6b and c, respectively. Figure S6d displays the evidence of the Cu 2p core level across the binding energy of 925-965 eV indicated the presence of Cu(II) oxidation state. Here, the two peaks centered at 933.60 eV and 953.30 eV are correspond to 2p$_{3/2}$ and 2p$_{1/2}$ core levels, respectively. In addition, the accompanying satellite peaks (943.70 and 961.75 eV) are also observed. In addition, we noted the presence of Zn 2p and Cd 3d core levels at their respective samples as displayed in Figure S6e and f, respectively. Furthermore, peak fitting of the Cu 2$p_{3/2}$ peaks revealed that the atomic ratio analysis exhibited a composition profile of approximately 79.07% Cu$^{2+}$ and 20.93% Cu$^+$ (See Supplementary Information, Figure S7). This strengthen the hypothesis that the chemical state of Cu$^{2+}$ serve as the prominent governing oxidation state in this compound.

Finally, we examined the presence of the allowed resonant transition across near-edge region with respect to the absorption threshold using resonant photoemission spectroscopy in (MA)$_2$CuCl$_4$ (Fig. 4). As we vary photon energy across the resonant C K-edge energies, we are able to probe the accessible energetic transition of 2p-3d excitation threshold. A resonant photoemission signal arises due to a manifestation of the interference effect between indirect (core – hole) and direct valence band processes The former represents (3d$^n + h\nu \rightarrow 3d^{n-1} + e^{-}$), whereas the latter [3d$^n + h\nu \rightarrow 3p^5 \ 3d^{n+1} \ (or \ 3p^5 \ 3d^{n+1}) \rightarrow 3d^{n-1} + e^{-}$]. Here, we emphasize in the C K-edge to illustrate the formation of an energetically charge carrier excitation from 1s to the lowest unoccupied state of (MA)$_2$CuCl$_4$. 
Figure 4. Resonant photoemission spectra of (MA)$_2$CuCl$_4$ close to carbon K-edge absorption threshold (~285.70 eV). a) ResPES wide scan from 280.00 eV – 290.40 eV. b) Selected ResPES region close to the on-resonant transition regime.

Figure 4 highlights the ResPES spectra of (MA)$_2$CuCl$_4$ with photon energy scan from 280 eV (off-resonance), across the 284.75-285.90 eV (on-resonance), towards higher photon energy up to 290.4 eV (off-resonance). Here, we identify a participator decay as a small peak near $E_F$ leading structure, centered at 2.14 eV (dot symbol) that remains fixed within the on-resonant regime. In addition, the occurrence peaks at 15.24 eV (club symbol) and 23.29 eV (diamond symbol) are assigned as spectator decay, as their peaks position varies with incident photon energy. The orbitals associated with these peaks are Cu 3$d$ (diamond), a mixture between Cl 3$s$ and Cu 4$s$ (club), and Cl 3$p$ (dot). Here, the difference between on- and off-resonance spectra indicates that the excited states are localized in C atoms and that they hybridize with Cl valence states. Thus, the resonance peak indicates that excited C atoms undergoes a charge transfer event (i.e. diamond and dot symbol) that spans from the organic molecules to the inorganic layered perovskite components. This is consistent with previous studies of the dominant orbitals near the valence (Cl 3$p$) and conduction band (Cu 3$d$)\(^9\). Since the energy shift of the peak occurs at the C K-edge (1$s$), this suggests C 1$s$ states also contributes to the valence and conduction band and are localized at the methylammonium molecules\(^8\). Substitution of the B-site in (MA)$_2$CuCl$_4$ to Cd and Zn also show similar trends of resonance spectra differences, suggesting that a similar charge transfer mechanism is occurring in other to (MA)$_2$BCl$_4$ (Fig. S8).
D. Spectroscopic Ellipsometry

![Spectroscopic Ellipsometry Graphs]

Figure 5. Optical properties of (MA)$_2$CuCl$_4$ probed by Spectroscopic Ellipsometry. Complex dielectric function comprises of a) real ($\varepsilon_1(\omega)$) and b) imaginary part ($\varepsilon_2(\omega)$). Through $\varepsilon(\omega)$, we calculated the (c) Reflectivity at normal incidence, (d) Loss function ($-\text{Im}[\varepsilon^{-1}]$), (e) absorption coefficient (with experimental absorption spectra (a.u.) in green), and (f) Tauc plot analysis with 2.91 eV x-intercept.

Finally, using the previous discussion on the optical and the electronic structures of (MA)$_2$CuCl$_4$, we want to validate them using SE and at the same time, we explain the physical phenomena related to the plasmonic effect. We have measured SE responses of (MA)$_2$CuCl$_4$ that were carried out at room temperature in three different incident angles with a fixed polarized light source. Here we noted that the intensity and phase difference of the reflected light were measured as $\Psi(\omega)$ and $\Delta(\omega)$, respectively. An optical model is generated from Kramers-Kronig consistent functions such as Tauc-Lorentz and PSEMI-TRI to fit the aforementioned SE values. The generated dielectric function from SE spectra is considered to be the most direct optical method as the technique measures both the real and imaginary part of the dielectric function$^{26, 50}$. The fitted data that corresponds to the complex dielectric function $\varepsilon(\omega)$ of the (MA)$_2$CuCl$_4$ film can be used to calculate the absorption coefficient, loss function, and reflectivity as shown in Fig. 5 a-f. Thus, complex electronic correlations can be interpreted through the detection of excitons, optical transitions, and spectral weight transfers$^{24, 28, 41}$. 
From our fitted $\varepsilon(\omega)$, it is shown that the onset of absorption was estimated at approximately 2.4 eV with a lack of a Drude-like peak in $\varepsilon_2(\omega)$. More importantly no crossing of zero value in $\varepsilon_1(\omega)$ was observed. Here, it can be considered that the hybrid perovskite possess a similar fingerprint as a semiconductor. A linear extrapolation of the Tauc plot allow us to estimate the band gap to be $\sim$2.91 eV (Fig. 5f). This result is in agreement with the previously reported value obtained by theoretical density functional theory (DFT) calculations and absorption measurements\textsuperscript{33, 49}.

Above the band gap regime, it turns out that the imaginary dielectric function $\varepsilon_2(\omega)$ reveals two significant absorption peaks which were observed at 3.16 eV (peak A) and 4.16 eV (peak B). Such high intensity absorption peaks are correspond to a dominant optical transition, however, this feature can be associated to the indication of inter-band, intra-band, excitonic, or other plausible transitions. To deconvolute these transitions, we plotted LF as shown in Fig. 5d in which two peaks at 3.28 eV (peak A') and 4.26 eV (peak B') were spatially resolved. Cortecchia et al. assigned these peaks as charge transfer/interband transitions originating from the halide bands (Cl) to the transition metal (Cu)\textsuperscript{49}. However, the LF peaks (A' and B') are blue-shifted with respect to the $\varepsilon_2(\omega)$ peaks (A and B), and moreover this trend is coincided with the minima in the reflectivity spectrum. We conclude that peak A' and B' can be assigned as plasmonic excitations\textsuperscript{28}. Moreover, we argue these prominent signatures as a manifestation of the unconventional plasmon peaks since typical conventional plasmons is accompanied by the presence of a zero-crossing in $\varepsilon_1(\omega)$ that typically can be found in a low-correlated gold\textsuperscript{51}.

To confirm our findings, we interpret several possibilities that could promote these unique optical excitations by referring to the plausible characteristics A' and B' peaks. First, we consider that spin-orbit coupling contributions can be safely eliminated since the peak separation between A' and B' is very large compared to typical spin orbit coupling separation of $\sim$200 meV\textsuperscript{52, 53}. Second, phononic peaks are commonly found below than 1 eV which is far beyond the range of the observed peaks here. Third, excitons are categorized based on their signature of asymmetric line shape in the absorption and optical conductivity. Thereby its absorption peak increases progressively as the impinged photon energy increases. This is not the case in the observed $\varepsilon_2(\omega)$, as both peak A' and B' do not exhibit typical characteristics of the exciton line shape represent a sharp onset with gradual increase in $\varepsilon_2(\omega)$. Lastly, we revisited the extracted optical band gap using tauc plot that resulted an onset at 2.91 eV. Thus, any peaks above the optical band gap may originate from inter-band transitions. When comparing inter-band transitions in $\varepsilon_2(\omega)$ and LF spectra, the peak location should not experience any blueshift, i.e. exact photon energy both in $\varepsilon_2(\omega)$ and LF. Although energetically the position is above the band gap, peak
A’ and B’ could not be considered as interband transitions since their respective energy position experienced is blueshifted. In contrast, a shoulder close to peak A’ may originate from interband transitions since its peak position did not blueshift in the LF. Therefore, according to this qualitative approach we consider both peaks are indeed generated due to plasmonic excitations that are quasilocal and unconventional in nature.

Previous unconventional plasmons studies has lay a profound knowledge that the generated signature can be found in 2D inorganic layered perovskite in which the extra oxygen layers introduce strong correlated effects to the electronic structure. This is analogous to the hybrid perovskite system where the organic anions serve as a potential barrier in similar fashion as oxygen layer in the former inorganic perovskite. In the case of (MA)$_2$CuCl$_4$, the electrons in the 2D inorganic layer is confined to the CuCl plane resulting in a highly correlated system, which is likely the cause of the unconventional plasmons we observe in the loss function. However, unlike the inorganic perovskites, methylammonium moiety is prone to lattice distortions thereby would impact the perovskite optoelectronic properties, such as self-trapped exciton (STE) emission in photoluminescence studies. In order to investigate the plausible role of lattice distortions and excitonic feature in the optical spectra, we therefore compare the unconventional plasmons signature of (MA)$_2$CuCl$_4$ with previous reports. It turns out that the unconventional plasmons in (MA)$_2$CuCl$_4$ exhibited significant low loss, as shown in Fig. 1, where the plasmons peaks intensities of A’ and B’ are eight times lower compared to gold. We determined the free electron scattering ($1/\tau$) and plasmons dephasing time ($T_2$), based on the FWHM of the plasmonic peaks. Using Lorentzian function fitting, we obtain the FWHM of peak A’ and B’ to be ~0.38 eV and ~0.51 eV, respectively. Thus, the corresponding dephasing time are 3.43 fs & 2.60 fs and free electron scattering are 0.72 eV & 0.84 eV, where our values are in agreement with the previous reports of unconventional plasmons.

Interestingly, we noticed that the Lorentz fitting cannot model the LF in an accurate fashion since peak B’ is somewhat skewed to the left. Moreover, previous theoretical models of unconventional plasmons using Lorentzian oscillators show that they are symmetric and the intensity is proportional to the photon energy ($hv$). A skewed plasmonic excitation is commonly attributed to the multipole plasmonic excitations prevalent in 2D systems such as graphene, therefore we attempt to fit the skewed plasmonic peaks using an Exponentially Modified Gaussian function (EMG), where we find that the fit is improved significantly (Fig. S9). Thus, it suggests that these unconventional plasmons are slightly different that the plasmons in previous studies, which may be generated by the presence of organic compounds in 2D HOIPs. Here, we note that unusual behavior of plasmonic signature that clearly deviates from conventional plasmons, therefore further studies are needed to confirm in great details imparting the evidence of unconventional plasmons in 2D hybrid perovskites.
III. CONCLUSION

We have studied the optical and electronic properties of (MA)$_2$CuCl$_4$ and other B-site substituted hybrid organic perovskites ((MA)$_2$CdCl$_4$ and (MA)$_2$ZnCl$_4$) through several combined optical and high-resolution photoemission techniques. Photoluminescence (PL) measurements of (MA)$_2$CuCl$_4$ confirms a broadband PL emission originating from self-trapped excitons (STE), due to soft crystal structure and lattice distortions. In addition, NEXAFS and ResPES highlight the coexistence of anomalous participator and spectator decay in the resonance regime, indicating a charge transfer between carbon atoms originating from MA moiety and the inorganic sites. Through SE measurements, we report the existence of unconventional plasmons in (MA)$_2$CuCl$_4$ in the visible-UV range. These complex interactions and correlation effects are governed the observation of the unconventional plasmons, originating from the contribution of organic molecules manifested as asymmetric and broad FWHM signature. From this study, we shed some light that hybrid perovskite materials are not only act as efficient emitters but these emergent materials could be promising in terms of plasmonic platforms for light-matter interactions. Such benefit that reside in one type of materials will simplify the material integration for efficient light emitting devices or lasers.

SUPPLEMENTARY MATERIALS

See supplementary materials for the synthetic route of (MA)$_2$CuCl$_4$ fabrication, experimental methods, XRD, SEM, AFM micrograph, steady-state photoluminescence and time-resolved PL spectra, Raman spectra, XPS, an overview of RePES of (MA)$_2$CuCl$_4$, NEXAFS of (MA)$_2$CuCl$_4$, XPS Cu $2p_{3/2}$ deconvolution peak. Loss function fittings and the corresponding statistics and the extracted resonant transition peak from NEXAFS measurements.

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