

Switching between spectral broadening and narrowing of the exciton absorption band of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film on altering the polarity of an applied electric field

Kamlesh Awasthi,^{1,2} Kannakutty Kala,¹ Shailesh Rana,¹ Eric Wei-Guang Diau^{1,2,a)}, Nobuhiro Ohta^{1,2,a)}

¹Department of Applied Chemistry and Institute of Molecular Science, ²Center for Emergent Functional Matter Science, National Chiao Tung University, 1001 Ta-Hsueh Rd., Hsinchu 30010, Taiwan.

^{a)}Authors to whom correspondence should be addressed: diau@mail.nctu.edu.tw and nohta@nctu.edu.tw

Abstract

The electric field-induced broadening and narrowing of an exciton absorption band have been observed to depend on the polarity of the applied electric field for methylammonium lead triiodide perovskite (MAPbI_3) as a thin film sandwiched between a conducting film of fluorine-doped tin oxide (FTO) and an insulating film of poly(methyl methacrylate) (PMMA). The width of the absorption band increased or decreased when the direction of the applied field was toward FTO or PMMA, respectively, indicating that the spectral broadening and narrowing becomes switchable on altering the direction of the applied electric field. When titanium oxide (TiO_2) in a compact layer was introduced between the MAPbI_3 and FTO layers, the linear electric-field effect that depended on the polarity was either not observed or decreased significantly, although the quadratic field effects on the exciton absorption band were similarly observed with or without the TiO_2 layer.

Organic-inorganic halide perovskites (PSK) are promising materials of great interest for fundamental research and for applications in next-generation optical techniques. For solar cells made of methyl ammonium lead triiodide PSK (MAPbI_3), the generated photocurrent is switchable repeatedly on applying a small electric field in a specific direction. This photovoltaic performance was associated with an ion drift in the perovskite layers [1,2]. Switching of physical quantities such as electric current, absorbance or emission intensity on irradiation with visible light or application of an electric field is important for the design and development of novel photonic and optoelectronic materials and devices such as switches and modulators [3-6].

Exciton absorption and photoluminescence in PSK is controllable with an applied electric field through the modulation of the energy levels or the dissociation of electron-hole pairs produced on photoexcitation [7-15]. In a centrosymmetric or randomly distributed system, electric dipoles that have opposite directions invariably exist; on average the linear field effect on absorption spectra is cancelled. As a result, a field-induced spectral shift or broadening of the absorption spectra of bulk samples is typically obtained as a quadratic effect. The effects of an electric field on absorption spectra of PSK reported so far are concerned mainly with the quadratic field effect, from which the magnitude of the change in electric dipole moment and polarizability following excitation to the exciton band of MAPbI_3 film was estimated to be 2.4 D and negligible, respectively [11]. A linear Stark effect is expected in crystals and materials that lack a center of symmetry, but a linear field-induced band narrowing or band broadening has been reported in some semiconductor-based quantum wells [16-19]. The measurement of the linear effect of an electric field hence provides significant information about the electronic structure at the interface and about the interfacial interaction that might induce an observable non-centrosymmetric phenomenon.

Here we report a linear effect of electric field on the exciton absorption band of MAPbI_3 sandwiched between FTO and PMMA layers; this band narrows or broadens, depending on the

polarity of the externally applied electric field. We show also that this linear electric-field effect depends on the film composition; when a compact layer of TiO₂ was introduced between the MAPbI₃ and FTO layers, the linear field effect either disappeared or decreased significantly, in contrast for the case of the TiO₂ layer absent.

A polycrystalline thin film of MAPbI₃ sandwiched between layers of FTO and PMMA, hereafter referred as sample I, was prepared as reported previously [11]. Briefly, the MAPbI₃ solution was dropped on a FTO-coated glass substrate for spin coating at rate 5000 rpm for 15 s, in combination with chlorobenzene to promote the rapid nucleation. Similarly, a polycrystalline thin film of MAPbI₃ sandwiched between TiO₂ and PMMA films, hereafter referred to as sample II, was prepared on depositing a MAPbI₃ film on a compact TiO₂ film coated on a FTO-coated glass substrate. Then, an insulating layer of PMMA film was deposited on the MAPbI₃ film in both samples with a spin-coating method. Figure 1 shows the SEM images of samples I and II; the thickness of the TiO₂ film was ~60 nm. A semi-transparent silver (Ag) film of thickness ~25 nm was further deposited on the PMMA film with thermal deposition. It is noted that SEM images of the MAPbI₃ crystal surface show no significant difference in morphology between samples I and II. The FTO and Ag films served as electrodes for the electroabsorption (E-A) measurements. We measured E-A spectra with a spectrometer (JASCO EMV-100) on modulating the electric field with a sinusoidal AC voltage of frequency 1 kHz, as described previously [11]. Briefly, field-induced change in transmitted light intensity of excitation light (ΔI_{EX}) was measured with a lock-in amplifier at the first harmonic ($1f$) or second harmonic ($2f$) of the modulation frequency, together with transmitted light intensity (I_{EX}). Then, the field-induced change in absorbance was obtained from $-\frac{1}{\ln 10} \frac{\Delta I_{EX}}{I_{EX}}$ and $-\frac{2\sqrt{2}}{\ln 10} \frac{\Delta I_{EX}}{I_{EX}}$ for $1f$ and $2f$, respectively [20,21]. Applied electric field was estimated from the applied voltage, whose maximum was less than 30 V, divided by the distance between FTO and Ag films. The total thickness was determined by using SEM and profilometer [11]. Excitation light was irradiated

to the area of sample films in a size of ~ 4 mm x 4 mm. A fluctuation of the thickness measured for this area is less than 5 %. Then, the observed E-A spectra are regarded as an average for this area.

Figure 2 shows the absorption and E-A spectra of sample I. These E-A spectra were recorded with a field strength of 0.3 MV cm^{-1} in each direction, which was obtained by application of 23 V AC voltage, on monitoring the field-induced variation of the intensity of transmitted excitation light synchronized at $1f$ of the modulation frequency of the applied field. The E-A spectrum shown in Figure 2b was obtained on applying the electric field in the direction from Ag to the FTO film, whereas the E-A spectrum shown in Figure 2c was obtained with the electric field in the opposite direction, i.e., from FTO to the Ag film. These field directions are hereafter called positive and negative directions, respectively. As Figure 2a shows, the absorption spectrum is separable into an exciton band by assuming the Gaussian profile with 587 ± 40 cm^{-1} FWHM and a continuum band (e-h curve). As mentioned in our previous paper [11], the separation of both bands could be done through the integral method analysis of the E-A spectra observed on monitoring the signal at $2f$ of the modulation frequency of the applied electric field, i.e., by taking the first and second integrals of the E-A spectra. Both exciton and e-h bands severely overlap with each other. In such a case, the integral method is very useful to simulate the E-A spectra, as proposed in our previous paper [22]. A small peak at ~ 790 nm in the e-h curve shown in Figure 2a, which had no reproducibility, is regarded as an artifact, probably resulting from the contribution of the scattering and/or the Gaussian profile approximation for the exciton band. As shown in Figures 2b,c the observed E-A spectra show essentially the same shape in both field directions, but the sign was reversed; that is, the peak intensity of the E-A signal at the absorption maximum decreased with the positive direction but increased with the negative direction. The continuum absorption band resulting from an optical

transition of free carriers likely remains unchanged with the application of the electric field, which was also recognized for the E-A signals observed for the applied electric field at $2f$ [9,11].

Figure 3 shows the E-A spectra monitored at $1f$ of the applied electric field with different strengths in the range of $0.17 - 0.4 \text{ MV cm}^{-1}$ in both positive and negative directions. The spectral shape of the E-A spectra is independent of the strength of the applied field; only the magnitude of the E-A signal depends on the strength. Plots of the field-induced change in absorbance (ΔA) relative to the exciton absorbance (A) at the peak of the E-A spectra show that the E-A signal is linearly proportional to the strength (F) of the applied field, i.e., $\Delta A/A = kF$; $k = \pm 0.0027 \text{ MV}^{-1} \text{ cm}$, depending on the field direction. If the observed linear field effect on absorption spectra results from a Stark effect, ΔA as a function of applied field strength is expected to be plotted as a linear function of F , in agreement with Figure 3b, but the shape of the E-A spectra should resemble the first derivative of the absorption spectra, which results from the field-induced spectral shift. Such a Stark shift results from a difference in polarizable character between the ground and excited states of the absorption, $\Delta E = \Delta\mu F$; ΔE is the field-induced shift of the energy of the absorption transition and $\Delta\mu$ is the difference of electric dipole moment between the ground and excited states. Such a linear Stark effect was observed in an oriented molecular system such as a Langmuir-Blodgett film [23,24] or dye molecules ordered on a surface [25]. Build-in field may also induce a shift of the energy gap [18], resulting in the first derivative of the absorption spectrum. Figure 4 shows the spectral shift and broadening (narrowing) of the absorption band and the resulting difference of the spectra; the shape of the observed E-A spectra differs critically from that of the first-derivative spectrum resulting from the shift of the absorption spectra, indicating that the observed linear field effect did not arise from a simple linear Stark shift caused by the change in the electric dipole moment following absorption. If the field-induced change comes from the Franz-Keldysh (FK) effect [26], oscillation is expected to be observed in the tail of the band-to-band transition, i.e., in the tail of the continuum band

located above the bandgap [27], which usually changes the zero-crossing position in the E-A spectra with different field strengths [10]. It is noted that such an oscillation caused by KF effect was also observed in the absorption tail of CdS nanowire and nanobelt above the band gap through photoconductivity measurements [28]. In the present results, the E-A signals observed at the first and second harmonics of the modulation frequency were proportional to the first and second power of the applied field strength, respectively, and the spectral shape was not affected by the applied field, that is, the zero-crossing position is the same with different electric fields, indicating no FK oscillation. Then, it is unlikely that the observed field effect results from the FK effect. The observed shape of the E-A spectra is similar to that of the second derivative of the Gaussian absorption shape, which results from the spectral broadening and narrowing (cf. Figure 4 and Figures 2 and 3). Thus, the spectral width of the exciton absorption band of MAPbI₃ film is found to become larger and smaller, as the external electric field is applied with the positive and negative directions, respectively.

As shown in Figures 5a & 5c both the samples I and II show similar absorption spectra and similar $2f$ E-A spectra, where the magnitude of ΔA is proportional to the square of the applied electric field (see Figure 5d), as reported previously [11]. Nevertheless, the linear effect of electric field on the exciton absorption band was not observed in sample II (Figure 5b), in which a compact layer of TiO₂ was coated above the FTO layer. MAPbI₃ films show similar quadratic field effect, even with different underlayers, but the linear field effect differed critically for samples I and II. In some cases, a tiny contribution of a linear field effects was observed for Sample II, which might arise from a small thickness of spin-coated TiO₂ layers.

Ion migration is known to occur in the time scale of around few seconds to several minutes [29]. Modulation frequency of 1kHz was used in the present experiments, and so it is unlikely that ion migration can follow the modulation frequency. In fact, it was shown that field-induced ion migration could be neglected at a frequency of 1 kHz with a field strength of 0.4

MVcm⁻¹ in MAPbBr₃ [13]. Roiati et al. reported the E-A spectra of MAPbI_{3-x}Cl_x solid film sandwiched between mesoporous TiO₂ (mp-TiO₂) and PMMA film by applying an oscillating AC field with superimposed DC bias [7]. Only in the presence of DC bias, the linear Stark effect resulting from the spectral shift was observed, suggesting that ion migration induced by DC bias gives the linear Stark shift, which is completely different from the present linear field effect. In the absence of DC bias, field-induced change in E-A intensity was negligible, consistent with the present results. These results indicate that the present linear field effect observed in MAPbI₃ sandwiched between FTO and PMMA doesn't come from ion migration.

The mechanism of the present linear electric-field effects on the exciton absorption band observed for sample I, i.e., a MAPbI₃ film sandwiched between FTO and PMMA, is poorly understood. However, the present polarity-dependent electric field effect reminds the theoretical work reported by Ponomarev et al. [16] for the exciton absorption band of quantum wells (QW), even though the present MAPbI₃ film having a 3D network crystalline structure is in contact with an FTO film. According to their theory, an inhomogeneous broadening of excitons in QW results from the interfacial disorder of the well through varied roughness; the inhomogeneous broadening is affected by the applied electric fields. Apart from a quadratic field effect that causes spectral broadening of the exciton absorption band, the linear electric-field effect is considered to arise from the asymmetry between two interfaces of the well, which is manifested on the exciton bandwidth through varied interface roughness. Switching between broadening and narrowing of the exciton bandwidth was suggested to be possible on altering the direction of the applied electric field. Interface roughness in QW is considered to be caused by the formation of monolayer islands on QW interfaces that result in local changes in the QW thickness [16], and the field-induced change in spectral width of the exciton absorption band, including the absence and presence of the effect, is considered to depend on the interface roughness. Then,

the present results of the linear electric field effects of MAPbI₃ film may indicate that the interface roughness of MAPbI₃ film on FTO and TiO₂ is different from each other.

Another possibility for the linear Stark effect in sample I is the presence of an internal electric field due to a potential difference between the interfaces of the MAPbI₃ film. If the internal field (F_{int}) exists in the MAPbI₃ film sandwiched between FTO and PMMA, this field itself induces an altered spectral width of the exciton absorption band; the application of an external electric field (F_{ext}) of alternate direction might alter the spectral width in an opposite way because the total electric field (F_{total}) can be regarded as a sum of the internal field and the external electric field, i.e., $F_{\text{total}} = F_{\text{int}} + F_{\text{ext}}$. The presence of an internal electric field that produces spectral broadening in an exciton absorption band was reported for a thin GaN layer [19]; the carrier produced on illumination of the sample was reported to decrease the effective electric field acting on an exciton, resulting in a narrowed exciton absorption band. In fact, the internal field in MAPbI₃ solid film was derived to be $\sim 0.7 \text{ MV cm}^{-1}$ in the maximum [30], based on the reported doping carrier density, the relative permittivity of perovskite layer, and the effective mass $0.2 m_0$ of electron and hole [25,31,32]. If F_{int} is 0.7 MVcm^{-1} and F_{ext} is 0.3 MVcm^{-1} , the total field becomes 1 MVcm^{-1} in the positive field direction and 0.4 MV^{-1} in the negative field direction; the field increases and decreases by 0.3 MVcm^{-1} , respectively, depending on the polarity. If the linear electric-field effect observed in sample I is caused by a synergistic effect between internal field and external field, however, the question remains why the field-induced spectral broadening or narrowing on altering the applied field direction was not observed in sample II. TiO₂ layer might weaken or change the nature of electric field in some way. For example, F_{int} may be affected by application of external electric field, resulting in the cancellation of the applied electric field on the surface. To understand the appearance and disappearance of the present linear E-A signal, further study including the measurements with other interface materials is necessary.

In conclusion, a linear electric field effect on exciton absorption spectra which differs critically from the conventional Stark shift has been observed for a MAPbI₃ film sandwiched between FTO and PMMA layers (sample I); the exciton absorption band becomes broader or narrower, depending on the direction of the externally applied electric field. This field-induced broadening or narrowing of the absorption band is switchable on altering the polarity of the applied electric field. In contrast, with an additional TiO₂ interfacial layer (sample II), the linear electric-field effect on the absorption spectra was not observed or minuscule. The linear electric-field effect on the exciton absorption profile of MAPbI₃ might be interpreted in terms of an interface roughness of the MAPbI₃ film at the FTO surface or the synergy effect between internal electric field generated in the MAPbI₃ film and applied electric field. However, further study is necessary to elucidate the mechanism. According to our observed linear electric-field effect on the exciton absorption profile, a switching device controlled with the polarity of the applied electric field might be feasible.

Acknowledgements

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Data Available Statement

The data that supports the findings of this study are available within the article.

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Figures

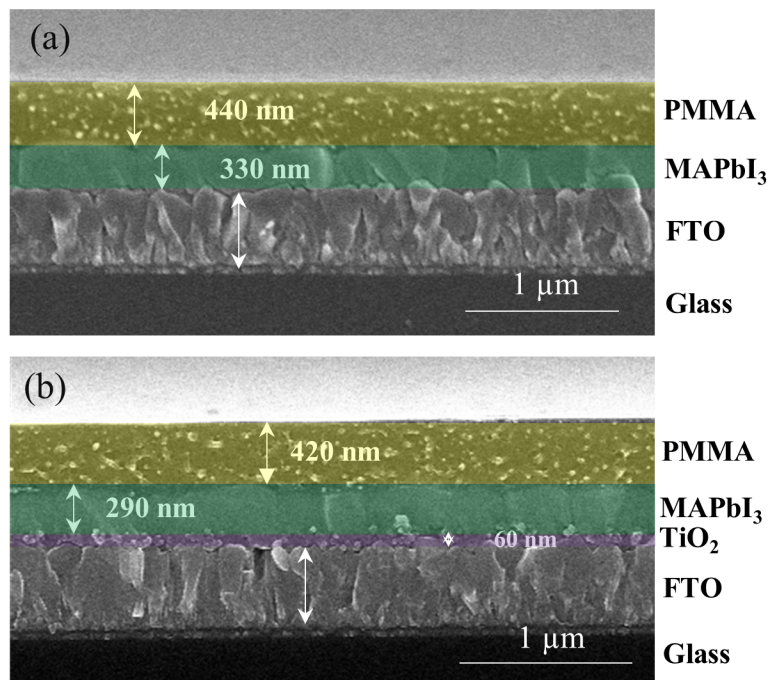


Figure 1. SEM images of the layer structures of (a) FTO/MAPbI₃/PMMA (sample I) and (b) FTO/TiO₂/MAPbI₃/PMMA (sample II).

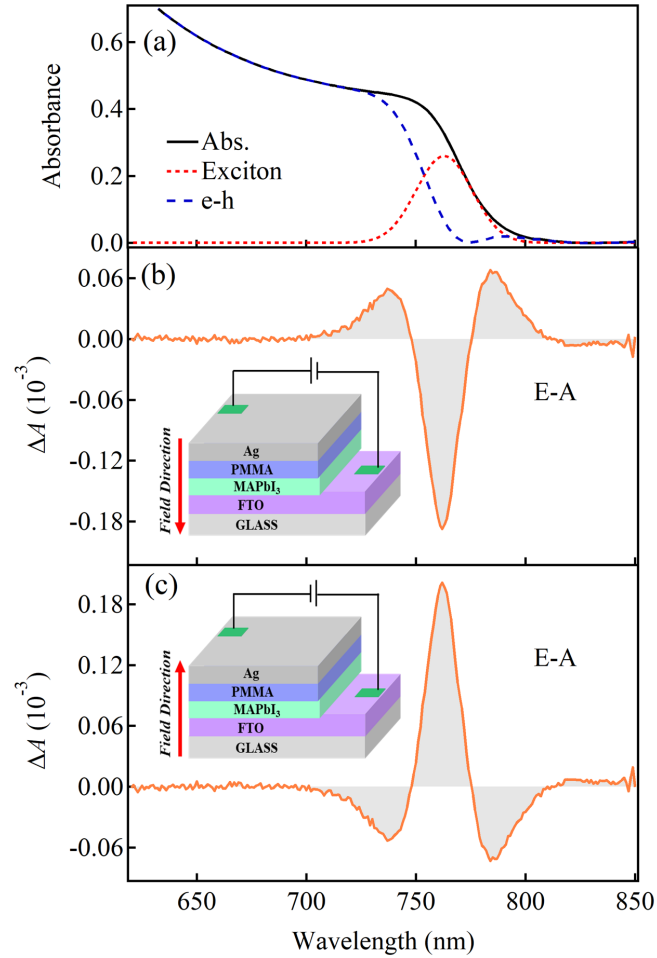


Figure 2. (a) Absorption spectra (solid line) of MAPI₃ films composed of an exciton transition (red dotted line) and a band-to-band transition (blue broken line), (b) E-A spectrum observed at $1f$ with field strength 0.3 MV cm^{-1} with field direction from Ag to the FTO electrode, (c) E-A spectrum observed at $1f$ with field direction from FTO to the Ag electrode. The schematic illustration of the sandwich films of MAPbI₃ perovskite (sample I) and the direction of the applied electric field are shown in (b) and (c).

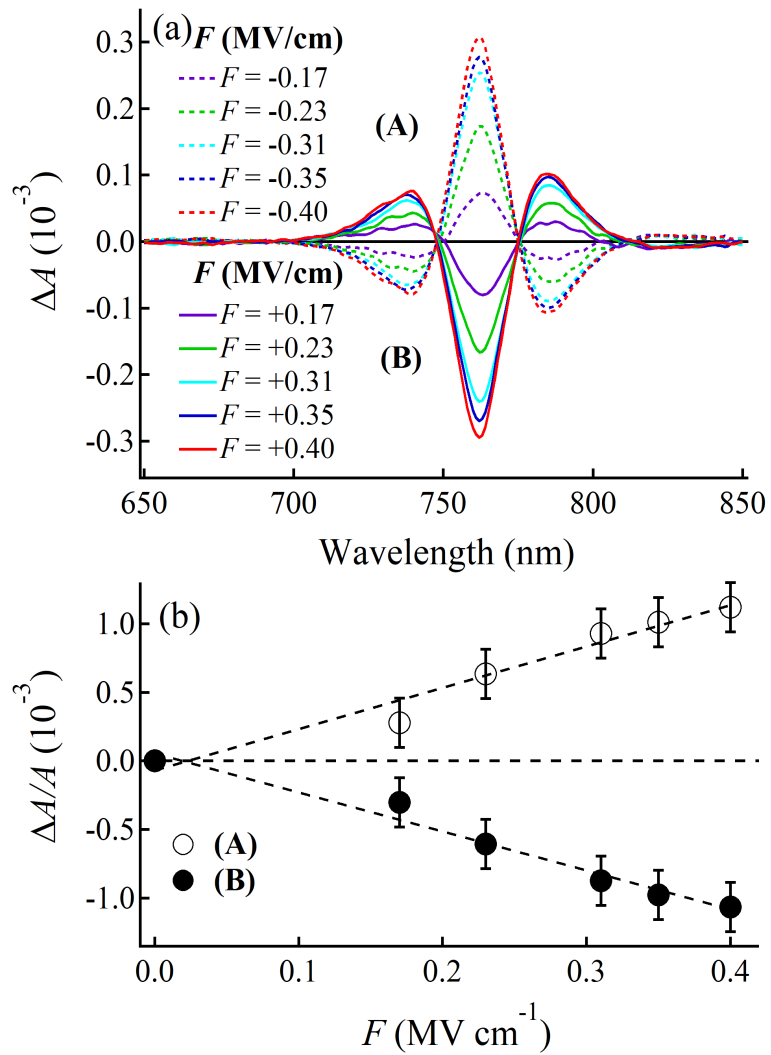


Figure 3. (a) Dependence on field strength of E-A spectra of sample I observed with negative (A) and positive (B) field directions and (b) plots of the field-induced change in absorbance relative to the absorbance at zero field as a function of strength of the applied field.

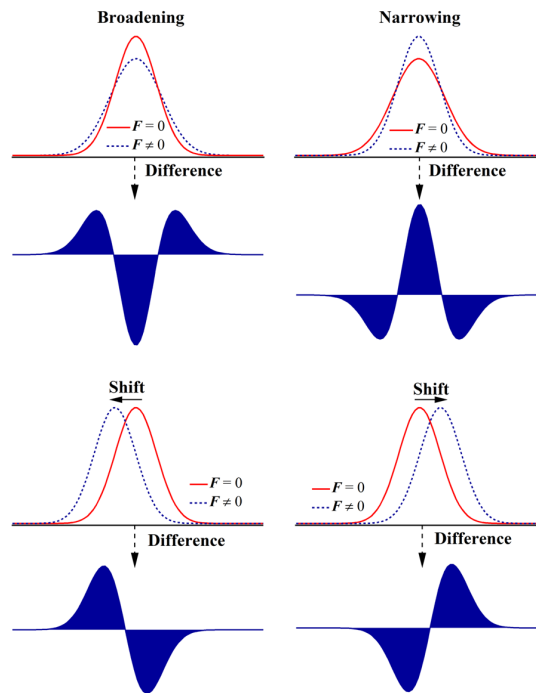


Figure 4. Schematic illustration of field-induced spectral broadening (upper left), narrowing (upper right), and the field-induced blue (lower left) and red (lower right) shifts of the spectra, with the difference between the spectra after and before application of the electric field.

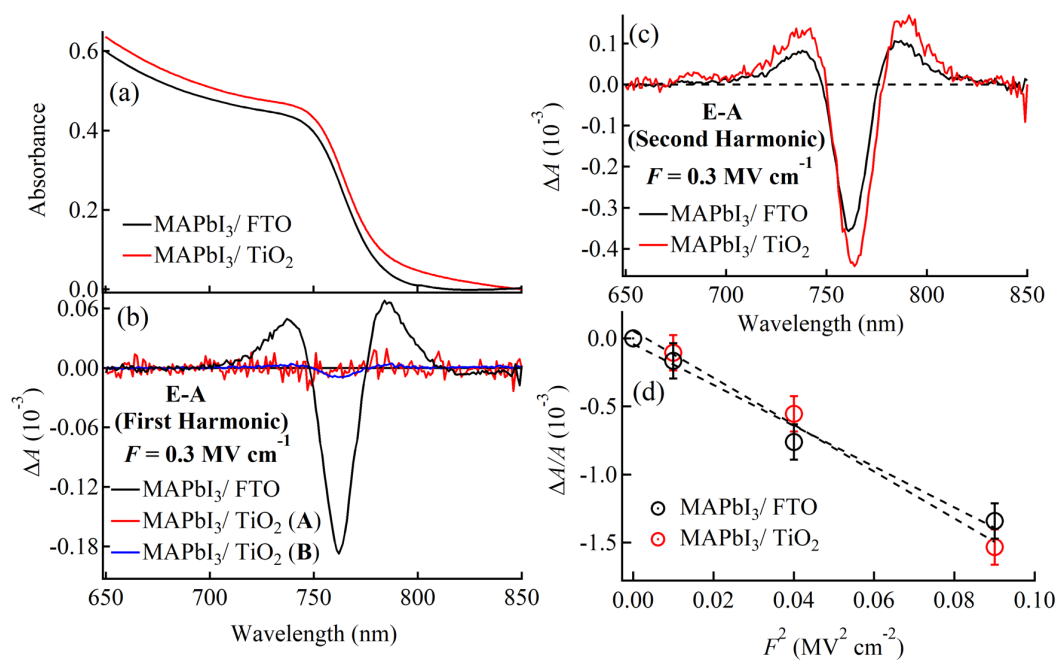


Figure 5. (a) Absorption spectra of MAPbI₃, (b & c) E-A spectra monitored at the first harmonic and at the second harmonic of the modulation frequency of the applied electric field, respectively, with different film configurations, and (d) plots of $\Delta A/A$ monitored at the second harmonic of the modulation frequency as a function of the square of the applied electric field at the minimum peak of the E-A spectra. Spectra in (b) shown in red and blue were obtained for the MAPbI₃ film sandwiched between TiO₂ and PMMA films with two samples, of which the thicknesses of TiO₂ layer might differ. E-A spectra in (b) and (c) were obtained with a field strength of 0.3 MVcm⁻¹.