**Response to reviewers’ comments of manuscript NCOMMS-17-20879 “Bimolecular Recombination In Methylammonium Lead Triiodide Perovskite: An Inverse Absorption Process” by Davies et al.**

We thank the three referees for their thorough and careful reading of our manuscript, and their suggestions for aspects that would benefit from clarification or elaboration. The referees generally acknowledged the high importance and broad interest of the work, and made a number of comments and suggestions for change.

We have thus modified the manuscript to take onboard all of the referees’ suggestions, and believe that taken together they strengthen the results in our manuscript. We hope that following our changes and responses summarized below, this revised article will now be suitable for publication in Nature Communications.

We address in detail each point raised individually below; verbatim referee comment is shown in **bold**, with our response in normal font below each comment. New/old manuscript text is given in italics and quotation marks, changes to the manuscript are summarized in red.

**Response to Referee 1**

**The manuscript “Bimolecular Recomination in Methylammonium Lead Triiodide Perovskite: An Inverse Absorption Process,” by Davies et al. describes a combined theory-absorption spectroscopy study of bulk CH3NH3PbI3 perovskite films. The authors utilize carefully measured reflectivity and transmission measurements collected at temperatures between 50 K and 300 K to measure the effective coupling between the ground and excited state electronic configurations. By doing so, the authors seek to model bimolecular recombination as an inverse absorption process. They are largely successful and argue for an elegant and simple solution to a process for which other authors have invoked some rather exotic physical phenomena. I find the arguments largely compelling and am certain they will be of significant interest to the community.   
  
My main issues with the manuscript largely revolves around the importance of the Mott density, and the relevance of the ground state (single excitation) absorption spectrum on obtaining quantitative consistency with the recombination rates. A couple points and suggestions below:  
  
1) Page 11, second paragraph, last sentence. The authors state that the Mott density is “…distributed about 10^17 cm^-3…” which is technically true. However, as the authors accurately point out in the supporting information, the Mott density is an exceptionally poorly defined quantity, with variation (depending on the equation) of more than 2 orders of magnitude. The authors’ statement is factually correct and they thoroughly and carefully walk through the relevant issues in SI, but this reviewer feels that the discussion in the manuscript does not adequately reflect the uncertainty in this important parameter. I strongly suggest the authors expand this discussion and highlight the issues with defining a Mott density and interpreting transient spectroscopies within its context.**

Author reply: We are in full agreement with the referee that the Mott density is intrinsically poorly defined. We are also very happy to comply with the referee’s request to add more discussion on this issue to the main article. In addition to our current detailed review in the Supplementary Information, we have now expanded the discussion in the main text to convey the uncertainty in the Mott density and help clarify this issue to the reader.

Changes made:

On page 11 paragraph 2:

Added after: [*… is the relevant quantity.*]

“The Mott density nM places a quantitative value on the transition from an insulating gas of excitons at lower densities to a metal-like state of an electron-hole plasma at high charge-carrier densities[SI ref 33]. The electrostatic force between charged particles is a continuous function of their relative distances to each other, therefore it is intrinsically challenging to define a distinct density at which a Mott transition occurs.

Hence a wide range of expressions for the Mott density have been proposed, which depend on different model assumptions and complexities, and whose validity is also temperature dependent. A detailed discussion and literature summary for a variety of models can be found in the Supplementary Information. To represent the variety of such models, we evaluate the Mott density as a function of temperature,39 based on different expressions and using values…. ”

**2) A more significant point regarding the Mott density and its relevance to the primary conclusions of the manuscript: The authors use bimolecular rate constants obtained from power-dependent transient spectroscopies performed in reference 17. In that manuscript, the authors globally fit a series of kinetic decay traces spanning ~ 2 orders of magnitude of carrier density, to extract the bimolecular recombination rate constant. While this approach is standard, the method implicity assumes that the rate constant does not vary across the measured carrier density (i.e. it is constant). However, one of the main conclusions of this manuscript is the importance of screening effects (from a high carrier density) to the reduction of the bimolecular rate constant. Thus, one must interpret the results of the current manuscript to imply that, experimentally, k2 must in fact increase as the initial carrier density decreases, i.e. k2 would trend from the upper curve to the lower curve of figure 3b as the initial carrier density increases. Given how close the authors are to the Mott Density (whatever it may be, see above), and the importance of screening effects for determining which is the “correct” absorption spectrum to use, I feel there needs to be further discussion addressing this apparent contradiction, and perhaps a few hypothetical checks of the arguments made in support of the main conclusions to ensure they are self-consistent.**

Author reply:

The referee makes a very insightful question on the presence of screening in the transient measurements and we agree that this would be useful to clarify in the main text. The transient measurements we compare our calculations against were taken for 6 different excitation fluences spanning 2 orders of magnitude. These data had been fitted globally in the standard way the referee mentioned, that is, based on a bimolecular recombination rate constant, k2, and an Auger recombination rate constant k3, (the monomolecular term, k1 had been fixed by alternative, independent measurements and was found to be too low to contribute over the 2ns window these measurements examined). Therefore, with only two free parameters plus a third (amplitude scaling) an excellent fit of the model with the data was obtained, as can be seen in the original article by Milot et al. [http://onlinelibrary.wiley.com/doi/10.1002/adfm.201502340/abstract]. Such excellent fits to multiple transients with few parameters suggests that k2 must in fact be time-independent and fluence-independent and hence a distinct Mott transition cannot lie within the fluence range explored in these measurements.

The numerical agreement we find in our study between values of k2 and the unscreened values calculated from the Roosbroeck-Shockley relation further suggests that these transients are taken for charge-carriers below the Mott density. We note that this conclusion is compatible with other studies that seem to suggest that in these materials screening is not present until much higher charge-carrier densities than those employed in these transient measurements. For example, a recent study of terahertz conductivity in MAPbI3 [https://www.nature.com/articles/ncomms15565] was able to directly observe snapshots of excitonic Rydberg states at excitation fluences that were one order of magnitude greater than the highest fluence used in the transient measurements we analyze here. If the charge-carrier density had been greater than the Mott density then the exciton would not have been observable, hence this gives conclusive evidence that the transients against which our calculations are referenced must have been acquired at charge-carrier densities that lie below the Mott density.

We agree with the referee that this aspect would benefit from further clarification and have now added further comment to our article.

Changes made:

On page 12 paragraph 2:

Changed: “As suggested previously2 and described in detail in Supplementary Information, this case applies at charge-carrier densities above ∼1015–1017 cm-3 for typical MAPbI3, which come near the Mott density within our observation regime (Figure S6d) and therefore small Coulomb-screening effects may already be present. Hence our analysis clearly supports the notion of an inverse absorption process leading to bimolecular recombination in CH3NH3PbI3.”

To: “As suggested previously2 and described in detail in Supplementary Information, this case applies at charge-carrier densities above ∼1015–1017 cm-3 for typical CH3NH3PbI3, which may potentially come near the Mott density (Figure S6d). However, a recent study [L. Luo et al., Nat. Commun. 8, 15565 (2017)] reported the direct observation of excitonic Rydberg states following excitation with fluences one order of magnitude higher than the highest fluence utilized for the transients against which we reference our calculated values of k2 here. We therefore conclude that the most adequate scenario for comparison is with values obtained from the Coulomb-enhanced (unscreened) absorption coefficient, for which Figure 3b also indicates best agreement. Hence our analysis clearly supports the notion of an inverse absorption process leading to bimolecular recombination in CH3NH3PbI3.”

**Response to Referee 2**

**The authors carried out a combined experimental/simulation study of the relation between**

**absorption and bimolecular recombination in MAPI. Their main finding is that MAPI obeys the van Roosbroeck-Shockley relation, relating the radiative emission by free carrier recombination to absorption. Absolute values of k2 but also its dependence on temperature are fully reproduced by applying the van Roosbroeck-Shockley relation to the temperature dependent free carrier absorption spectra. In addition, sophisticated GW calculations are performed to reproduce the measured absorption spectra, and good agreement to the shape and strength of the experimental absorption coefficient spectrum is obtained when considering higher energy transitions, the non-parabolicity of the bands, and also a slight dependence of the transition matrix element on energy.**

**The present paper is, undoubtful, of highest quality, written by world-class scientists. There are, however, two important issues which the authors need to consider in the revised version of the paper.**

**1. The main objective of the paper is to show that bimolecular recombination is the inverse to free carrier absorption in MAPI. In my opinion, this result was actually expected from previous work by other groups. Importantly, several author employed Rau’s reprocity to reproduce the Voc of MAPI and other hybrid-perosvkite solar cells from the EQE\_PV spectra, with excellent agreement between the prediction and the experimental findings (see e.g. [K. Tvingstedt et al., Sci. Rep. 4, 6071 (2015).]. Rau’s reciprocity is a similar to the van Roosbroeck-Shockley, but it also takes into account non-unity efficiencies for charge generation and free charge recombination. As Rau’s reciprocity relies on the assumption that all photon emission comes from free carrier recombination, and that free carrier recombination is the inverse process of free carriers formation by photon absorption, and MAPI obeys Rau’s reciprocity, the rate of radiative free carrier recombination must be given by the absorption. Therefore, the more relevant question to answer is whether all free carrier recombination is emissive, because its only then that k2 is equal to Rrad/(ni)2. The present study shows that this is the case, providing firm proof for the assumption that bimolecular recombination in MAPI is always radiative!**

Author reply:

We thank the referee for his/her positive evaluation of the quality of our work. With regards to the expectation of the result we reveal in our study, we emphasize that our finding that bimolecular recombination is the inverse process of absorption had not been deduced in previous works. Importantly, the numerical agreement of one VOC value using Rau’s reciprocity is not sufficient to show this relation either. VOC depends on many different factors including device architecture, layer morphology, contact layers, age of device, atmospheric exposure and more. As a result, the reasons for open-circuit losses are a subject of investigation in their own right in the perovskite PV community at the moment. Hence a single numerical co-agreement is not conclusive evidence of any relation between absorption and bimolecular recombination.

We also stress that while we agree with the referee that our finding is broadly sensible, the field has never-the-less been inundated with unusual and mostly quantitatively unverified alternative mechanisms for bimolecular recombination. Our work is able to strongly refute these and will therefore help to conclude this discourse in the literature. Referee 1 broadly agrees with our arguments here, pointing out that we *“are largely successful and argue for an elegant and simple solution to a process for which other authors have invoked some rather exotic physical phenomena. I find the arguments largely compelling and am certain they will be of significant interest to the community.”*. In summary, our article offers definitive evidence of the relation between absorption and bimolecular recombination, and details the physical significance of this relation in the context of future device fabrication. By performing a temperature dependent study, we are able to reveal an unambiguous and quantitative proof for the mechanism of bimolecular charge-carrier recombination and, as this Referee 2 points out, also firm evidence that bimolecular recombination in MAPbI3 is always radiative.

**There is a second question related to this finding, namely, whether other processes than free carrier recombination in the MAPI bulk (such as emission from defects) contribute to photon emission. A recent work by Felix Deschler however revealed an unambiguous second order relation between the PL emission rate and the carrier density in the device [J.M. Richter et al., Nat. Commun. 7, 13941 (2016).]. This result provides firm proof that photon emission origins exclusively from a two-body process, namely free carrier formation. In view of these findings, certain parts of the paper need to be reconsidered, with proper reference to the work cited above (and related work).**

Author reply:

We fully agree with the referee that the validity of the Roosbroeck-Shockley relation means that bimolecular recombination is a fully radiative process and we have now added a statement to point this out clearly. There are also some earlier works commenting on this matter that precede the paper by Richter (which is mainly on self-absorption effects), notably M Saba et al., *Nat. Commun.* **2014**, 5, 5049 and M B Johnston and L M Herz *Acc. Chem. Res.*, **2016**, *49* (1), 146–154 and these have now also been included in the citations along with Richter’s paper.

Changes made:

On page 13, added after: [*… that these processes can be seen as the inverse of absorption.*]

“and are fully radiative[CITATIONS].”

Added reference to the following CITATIONS:

M Saba et al., *Nat. Commun.* **2014**, 5, 5049

M B Johnston and L M Herz *Acc. Chem. Res.*, **2016**, *49* (1), 146–154

J.M. Richter et al., *Nat. Commun.*, 7, 13941 **(2016).**

T Crothers *Nano Lett.*, **2017**, *17* (9), 5782–5789

**2. My second remark concerns the simulation of the absorption spectra using GW. I actually**

**enjoyed reading this section but I wonder how (and whether) the results of this simulation**

**studies contribute to the main conclusion paper, which is the reciprocity between free charge**

**bimolecular recombination and photon absorption. If I understand correctly, k2 in Figure 3b**

**was calculated on the basis of the experimental absorption spectra (corrected for the**

**excitonic contribution), only, and the main input from the simulation work is the effective**

**mass of electrons and holes. I actually noticed that the agreement between the measured**

**absorption spectrum and the one calculated from GW is not that convincing when plotted on**

**the same energy scale, though the absolute absorption coefficient is rather well reproduced.**

**This decreapancy needs to be addressed in the revised version of the manuscript.**

Author reply:

We thank the referee for her/his positive comments about our ab initio calculations for MAPbI3. The referee is correct in stating that the values of k2 shown in Figure 3b were calculated from the van Roosbroeck and Shockley relation on the basis of the experimental absorption spectra. We have now made a short addition to the manuscript so that this is completely clear.

Changes made:

Caption of Figure 3:

Added after: [*...determined through the van Roosbroeck and Shockley relation*] from fits to the experimentally obtained absorption spectra [, *based on either the* …]

To clarify also the value added by these simulations, we note that they are extremely important in allowing us to both demonstrate the applicability of Elliott’s theory to the absorption edge and determine the values of the electron and hole effective masses. Elliott’s theory has recently been applied to hybrid perovskite absorption onsets but the deviations between experiment and theory has been poorly understood, with previous works ignoring the principle assumptions the model is based on. The calculations of the material allow us to probe each assumption and discuss the validity of the model for MAPbI3.

Changes made:

On page 9 Line 15:

Added “[*… coefficient spectrum of CH3NH3PbI3*.] Hence these ab initio calculations have enabled us to individually explore each assumption that Elliott’s theory is built on, allowing us to probe its validity for hybrid perovskite semiconductors. [*Overall, our analysis* …]”

To comment on the reasons for the discrepancies between the experimental and calculated absorption spectra we note that the main purpose of Figure 2d is to allow the reader to examine the differences between DFT and the GW method and show the scope of the modeling used (experimental data is already shown in Fig 1b). The GW and DFT based absorption spectra are calculated using the independent particle approximation. At this level of approximation the optical spectra are expected to be within a factor of 2 or 3 of the experimental spectra. There are two main reasons for the discrepancy between the calculated and experimental spectra, on which we comment here and have now added additional material to the main article and Supplementary Information.

Firstly, electron-hole interactions are not taken into account owing to the calculations being currently computationally intractable for MAPbI3. We had already included a comment to highlight this in the captions for Figure 2d, but we have now also pointed this out in the main text for clarification.

Changes made:

On page 9, changed “Comparison with experimental data (Figure 1b) shows that…” to

“Comparison with experimental data (αfree, Figure 1b) shows that…”

Secondly, calculating the dipole matrix elements directly from GW requires a self-consistent calculation of the quasi-particle wave functions, which is computationally prohibitive at the moment for a system of the size of MAPbI3. To overcome this bottleneck, we have taken advantage of the observation that quasi-particle and DFT wave functions are not significantly different (as discussed in Ref. 19 of the Supplementary Information), and calculate the dipole matrix elements only at the DFT level. Currently displayed in Figure 2d, is the GW absorption coefficient which uses the DFT dipole matrix elements rescaled by the difference in eigen-energies between conduction and valence bands (see Equation 3 of the Supplementary Information). In comparison with the experimental absorption coefficient, the scaled GW calculation overestimates the absorption coefficient. The correct value of the absorption coefficient for screened electrons and holes is most likely bracketed between the calculated absorption coefficient using the scaled DFT dipole matrix and the original DFT dipole matrix. To clarify this issue we have: (i) updated Figure 2d to show the absorption coefficient calculated by DFT, and GW for the cases of scaled and unscaled dipole matrix elements; (ii) extended the discussion in the Supplementary Information making all calculation very explicit; (iii) added a paragraph in the main text detailing the variants of the absorption coefficient and amended the relevant passages. These changes are detailed below:

Changes made:

On page 22

Updated Figure 2d:

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Caption replaced: [“*(d) Absorption coefficient spectrum calculated from density functional theory (DFT) calculations (red) and GW calculations (blue), performed within the independent-particle approximation (i.e. without considering electron-hole Coulomb interactions). Absorption coefficients have been scaled along the energy axis to make the onset coincide with the experimental value EG, but not scaled in the magnitude of the coefficient.”*]

With: “(d) Absorption coefficient spectrum calculated from density functional theory (DFT) calculations (black), and GW calculations (blue) within the independent-particle approximation (i.e. without considering electron-hole Coulomb interactions). We report results using scaled (solid) and un-scaled (dashed) dipole matrix elements, as derived using Equations 4 and 5 given in the Supplementary Information. The light blue region represents the uncertainty in the magnitude of the optical absorption spectrum owing to the approximate calculation of the dipole matrix elements. The functions have been shifted along the energy axis to make the onset coincide with the experimental value of EG.”

Changes made:

On page 22, caption for Figure 2c:

Added after: [“*… at different k-points in the Brillouin zone”*], “using Equation 3 of the Supplementary Information.” [~~and~~  *The blue lines show …*]

Changes made:

On page 9, paragraph 2:

Replaced: [“*Our rigorous evaluation of all factors contributing to the absorption allows us to derive the absorption coefficient spectrum entirely from ab initio calculations as shown in Figure 2d for both DFT and GW approximations. Spectra derived from DFT and GW calculations are shifted in energy to coincide with the extracted band gap but have not been scaled. Comparison with experimental data (Fig. 1b) shows that the calculations agree well with the experiment, suggesting that inclusion of band non-parabolicity, higher-lying transitions and the correct functional dependence of the matrix element allows an accurate evaluation of the free-charge absorption coefficient spectrum of CH3NH3PbI3.* ”]

With:

“Our rigorous evaluation of all factors contributing to the absorption allows us to derive the absorption coefficient entirely from ab initio calculations (see Supplementary Information), as shown in Figure 2d for both DFT and GW approximations. An accurate calculation of the absorption coefficient within the GW approximation requires the inclusion of the off-diagonal terms of the quasiparticle self-energy, which is computationally prohibitive for the case of CH3NH3PbI3. Instead, in Figure 2d we show two limits of the GW absorption spectra obtained using the dipole matrix elements calculated from DFT, both before and after scaling with respect to the quasiparticle transition energies (see Supplementary Information). Figure 2d shows that the absorption coefficient is sensitive to scaling, and can vary by up to a factor of 4, while the shape of the spectrum does not vary significantly. Moreover, it can be shown that the f-sum rule in these two cases is either overestimated, if the matrix elements are scaled, or underestimated in the unscaled case, consistent with the respective magnitudes of the absorption coefficient shown in Figure 2d. For this reason, we propose that the true absorption coefficient is bracketed by the scaled and unscaled GW spectra, which give good agreement with the experimental data (αfree, Figure 1b). This result indicates that the inclusion of band non-parabolicity, higher-lying transition and the functional dependence of the matrix element are fundamental for the accurate evaluation of the absorption coefficient in CH3NH3PbI3.” [*Overall ...*]

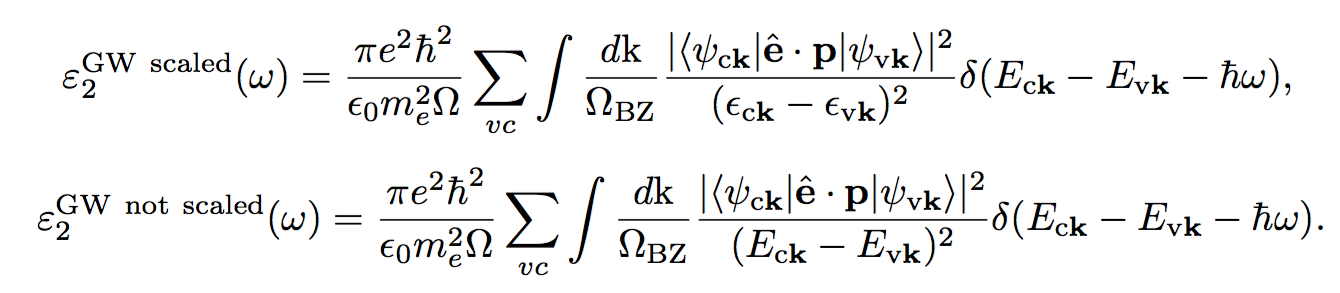
Changes made:

Supplementary Information on page 7, paragraph 2:

Replaced: [ “*The imaginary part of the dielectric function in this case becomes: [Equation 4]*” ]

With:

“For comparison, we calculate the GW optical absorption spectrum using either the scaled dipole matrix elements (Equation 3) or the dipole matrix elements calculated directly from DFT, using the following two expressions:”



**Response to Referee 3:**

**Dear Editor, the paper Bimolecular Recombination In Methylammonium Lead Triiodide Perovskite: An Inverse Absorption Process by Christopher L. Davies, Marina R. Filip, Jay B. Patel, Timothy W. Crothers, Carla Verdi, Adam D. Wright, Rebecca L. Milot, Feliciano Giustino, Michael B. Johnston & Laura M. Herz reports a detailed and accurate analysis of the bimolecular charge-carrier recombination in methylammonium lead triiodide perovskite. The work is based on the analysis of the absorption data measured on thermal evaporated thin films with tungsten halogen lamp as the illumination source. The absorption spectra are recorded at different temperatures and analyzed by using the Elliot's theory accouting for both excitons and hole-electron population.  
The important concept discussed in the paper is that the absorption from free (screened) electrons and holes must be increased by the Coulomb-enhancement factor ξ. The absorption coefficient, once rescaled, can be used to estimate the bimolecular recombination through Van Roosbroek relation (equation 2 and 31 of the SI). Such a methodological approach is clearly stated in the title as the recombination is described as the inverse absorption mechanism.  
The Authors claim that the enhancement of the optical absorption is mandatory to predict bimolecular recombination from absorption and to reconcile predicted values with experimental data. The enhancement is important particularly at low temperatures and low injection when the screening of photo-generated carriers is inefficient. The parameter is not a constant but it is extrapolated by fitting the measured absorption data.   
The paper is well written and performed competently but I don't think it is appropriate for Nature Communication.   
Though the paper contains interesting material, it is incremental with respect to state-of-the-art understanding of the hybrid perovskites. The Elliot's theory and the e-h+coulomb enhancement have been already reported in literature (see for example Ref. 53). Also the use of the absorption coefficient to estimate the bimolecular recombination was discussed in literature cited in the present paper. The picture supported by the present results is that the material behaves mainly as a standard inorganic semiconductor for which radiative recombination from free (though correlated or enhanced) hole-electrons is the limiting factor towards photoconversion.  
I think that the paper is more relevant from a methodological point of view with the supporting information containing material that should probably go in the main text in a regular article format. In conclusion, this is a good paper that deserves publication but I suggest an alternative long-format regular article.**

Author reply:

We thank the referee for his/her acknowledgement that the paper was interesting and well written. Regarding the Coulomb enhancement factor, the referee may possibly have perceived this to be a free parameter; however, it is actually a fixed function of energy determined by the extracted band gap and binding energy, and calculated using Equation 10 given in the Supplementary Information. We have now added a sentence in the main text to make this dependence clear to the reader.

Changes made:

On page 5:

Added after *[…by a factor ξ(E) beyond that expected for free electrons and holes (αC(E), red dashed line).]*

ξ(E) is the Coulomb enhancement factor derived from the values of the band gap and binding energy (see Equation 10 in the Supplementary Information) and is therefore not a free (independent) parameter of the model.

Regarding the novelty of our work, we emphasise that this is the first study to prove that bimolecular recombination in the hybrid perovskite is the reverse process of absorption, as described by the van-Roosboeck and Shockley relation. The field of hybrid perovskites has unfortunately been inundated with unusual and mostly quantitatively unverified alternative mechanisms for bimolecular recombination. Our work is able to strongly refute these and will therefore help to conclude this discourse in the literature. Referee 1 broadly agrees with our arguments here, pointing out that we *“are largely successful and argue for an elegant and simple solution to a process for which other authors have invoked some rather exotic physical phenomena. I find the arguments largely compelling and am certain they will be of significant interest to the community.”*. Our article offers definitive evidence of the relation between absorption and bimolecular recombination, and details the physical significance of this relation in the context of future device fabrication. By performing a temperature dependent study, we are able to reveal an unambiguous and quantitative proof for the mechanism of bimolecular charge-carrier recombination, which has been elusive in the literature to this present point.

The referee is of course correct in stating that Elliott’s theory had previously been used to model absorption spectra of hybrid perovskites, as we had ourselves pointed out in the main text. However, previous studies had found (as we did here) that there was a deviation between Elliott’s theory and the shape of the experimental absorption spectrum from ~200meV above the band edge. The reasons for such deviations were not understood, and therefore it was unclear if such a model could in fact be used to unravel the different contributions to the absorption in the way that is required to utilize the van-Roosbroeck and Shockley relation. By considering all the model assumptions of the theory (parabolic bands, only one conduction and valence band, constant electric-dipole moment) and using first principle calculations we were able to explain these discrepancies. Other groups had introduced non-parabolicity at the band edge however our calculations show that this cannot be the case. Also, efforts to introduce non-parabolicity to Elliott’s theory had failed to realize that the excitonic wavefunction solutions to the Schrodinger equation, critical to Elliott’s theory, would also need to be recalculated and therefore a simple modification to the final result of Elliott’s theory would have been completely invalid and resulted in inaccurate analysis. Therefore, our analysis was a crucial precursor allowing us to conduct the derivation of the bimolecular recombination rate constant from the absorption spectra.

The referee is also correct in acknowledging that a study we had cited had attempted to calculate the bimolecular recombination rate constant from an absorption coefficient, however this work was purely theoretical and utilized an absorption spectrum at a single temperature fully calculated from DFT. As the referee can see from our text below, the theoretical absorption coefficient has some margin of error, meaning that numerical agreement could never be reached with certainty in this approach. A fully theoretical approach can also, to date, not reproduce accurately the temperature-dependence of k2, as we have done here. In addition, DFT calculations also do not include electron-hole interactions and therefore excitonic effects and Coulombic enhancement will not be present in the simulated spectrum. As our study shows, these effects are highly important in order to accurately replicate the bimolecular recombination from absorption spectra. Therefore, a purely theoretical study is unable to present any proof a particular mechanism being in operation. In contrast, our study is based on actual, experimental verification of the van-Roosbroeck-Shockley relation, which is the only way in which this can be done with any certainty.

Considering the extended length of the Supplementary Information (31 pages) we believe that the current format is the most suitable for our work and will be more accessible to the wide audience of readers interested in these results.

**Additional points:  
• Why is not the GW based absorption reported together with experimental data? By comparing Fig.2 and Fig.1 it seems that the theoretical absorption (without enhancement) compares with coulomb enhanced curve. Is this the case? Please comment.**

Author reply:

The referee is correct that the theoretical absorption should be compared to the absorption spectra without enhancement. We apologize if this had not been clear from the text. The GW results were plotted alongside the DFT calculations to highlight the difference in absorption spectrum produced by the two methods and to allow an honest assessment of the work. The value of the first principles calculations was in explaining the validity range and limitations of Elliott’s theory and yielding accurate effective masses required for the calculations. The calculated value of absorption coefficient is slightly high when compared with the absorption spectra without Coulombic enhancement (αFree).

There are two main reasons for the discrepancy between the calculated and experimental spectra, on which we comment here and have now added additional material to the main article and Supplementary Information.

Firstly, electron-hole interactions are not taken into account owing to the calculations being currently computationally intractable for MAPbI3. We had already included a comment to highlight this in the captions for Figure 2d, but we have now also pointed this out in the main text for clarification.

Changes made:

On page 9, changed “*Comparison with experimental data (Figure 1b) shows that…”* to

“Comparison with experimental data (αfree, Figure 1b) shows that…”

Secondly, calculating the dipole matrix elements directly from GW requires a self-consistent calculation of the quasi-particle wave functions, which is computationally prohibitive for a system of the size of MAPbI3. To overcome this bottleneck, we have taken advantage of the observation that quasi-particle and DFT wave functions are not significantly different (as discussed in Ref. 19 of the Supplementary Information), and calculate the dipole matrix elements only at the DFT level. Currently displayed in Figure 2d, is the GW absorption coefficient which uses the DFT dipole matrix elements rescaled by the difference in eigen-energies between conduction and valence bands (see Equation 3 of the Supplementary Information). In comparison with the experimental absorption coefficient, the scaled GW calculation overestimates the absorption coefficient. The correct value of absorption coefficient for screened electrons and holes is most likely bracketed between the calculated absorption coefficient using the scaled DFT dipole matrix and the original DFT dipole matrix. To clarify this issue we have: (i) updated Figure 2d to show the absorption coefficient calculated by DFT, and GW for the cases of scaled and unscaled dipole matrix elements; (ii) extended the discussion in the Supplementary Information making all calculation very explicit; (iii) added a paragraph in the main text detailing the variants of the absorption coefficient and amended the relevant passages. These changes are detailed below:

Changes made:

On page 22

Updated Figure 2d:

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Caption replaced: [“*(d) Absorption coefficient spectrum calculated from density functional theory (DFT) calculations (red) and GW calculations (blue), performed within the independent-particle approximation (i.e. without considering electron-hole Coulomb interactions). Absorption coefficients have been scaled along the energy axis to make the onset coincide with the experimental value EG, but not scaled in the magnitude of the coefficient.”*]

With: “Absorption coefficient spectrum calculated from density functional theory (DFT) calculations (black), and GW calculations (blue) within the independent-particle approximation (i.e. without considering electron-hole Coulomb interactions). We report results using scaled (solid) and un-scaled (dashed) dipole matrix elements, as derived using Equations 4 and 5 given in the Supplementary Information. The light blue region represents the uncertainty in the magnitude of the optical absorption spectrum owing to the approximate calculation of the dipole matrix elements. The functions have been shifted along the energy axis to make the onset coincide with the experimental value of EG.”

Changes made:

On page 22, caption for Figure 2c:

Added after: [“*… at different k-points in the Brillouin zone”*], “using Equation 3 of the Supplementary Information.” [~~and~~  *The blue lines show …*]

Changes made:

On page 9, paragraph 2:

Replaced: [“*Our rigorous evaluation of all factors contributing to the absorption allows us to derive the absorption coefficient spectrum entirely from ab initio calculations as shown in Figure 2d for both DFT and GW approximations. Spectra derived from DFT and GW calculations are shifted in energy to coincide with the extracted band gap but have not been scaled. Comparison with experimental data (Fig. 1b) shows that the calculations agree well with the experiment, suggesting that inclusion of band non-parabolicity, higher-lying transitions and the correct functional dependence of the matrix element allows an accurate evaluation of the free-charge absorption coefficient spectrum of CH3NH3PbI3.* ”]

With:

“Our rigorous evaluation of all factors contributing to the absorption allows us to derive the absorption coefficient entirely from ab initio calculations (see Supplementary Information), as shown in Figure 2d for both DFT and GW approximations. An accurate calculation of the absorption coefficient within the GW approximation requires the inclusion of the off-diagonal terms of the quasiparticle self-energy, which is computationally prohibitive for the case of CH3NH3PbI3. Instead, in Figure 2d we show two limits of the GW absorption spectra obtained using the dipole matrix elements calculated from DFT, both before and after scaling with respect to the quasiparticle transition energies (see Supplementary Information). Figure 2d shows that the absorption coefficient is sensitive to scaling, and can vary by up to a factor of 4, while the shape of the spectrum does not vary significantly. Moreover, it can be shown that the f-sum rule in these two cases is either overestimated, if the matrix elements are scaled, or underestimated in the unscaled case, consistent with the respective magnitudes of the absorption coefficient shown in Figure 2d. For this reason, we propose that the true absorption coefficient is bracketed by the scaled and unscaled GW spectra, which give good agreement with the experimental data (αfree, Figure 1b). This result indicates that the inclusion of band non-parabolicity, higher-lying transition and the functional dependence of the matrix element are fundamental for the accurate evaluation of the absorption coefficient in CH3NH3PbI3.” [*Overall ...*]

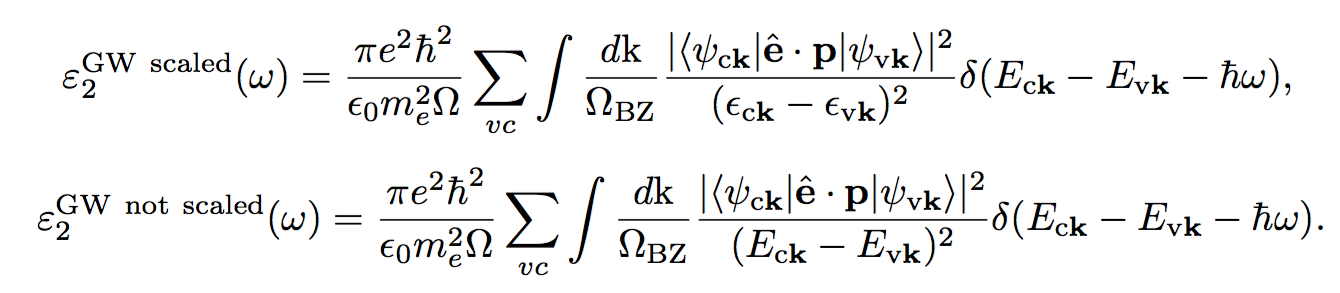
Changes made:

Supplementary Information on page 7, paragraph 2:

Replaced: [ “*The imaginary part of the dielectric function in this case becomes: [Equation 4]*” ]

With:

“For comparison, we calculate the GW optical absorption spectrum using either the scaled dipole matrix elements (Equation 3) or the dipole matrix elements calculated directly from DFT, using the following two expressions:”



**• It seems to me that despite the extensive GW analysis, the theoretical data used in the calculation of the radiative recombination are the effective masses within parabolic approximation. GW is used to validate the use of Elliot's theory and harmonic approximation. It is probably better to clarify this from the beginning of the paper. Despite the analysis is supported by ab initio GW data, nevertheless the enhancement factor cannot be determined a priori but it practically acts as a fitting parameter.**

Author reply:

We are in complete agreement with the referee that the GW analysis is used to validate the use of Elliott’s theory and define a range of energies over which the theory is applicable. As requested, we have now added a statement early in the article to clarify this fully right from the start.

Changes made:

On page 4 paragraph 2: Added after [*… With the help of insights gained from ab initio calculations*] “regarding the validity and applicability of Elliott’s theory to CH3NH3PbI3,” [we are able to …]

We would also like to clarify that the enhancement factor is not an independent fitting parameter, but rather a function of energy that depends on the binding energy and band gap, as detailed in the Supplementary Information pages 10 and 11. Successful fits to the measured absorption spectrum (αC) yield values for the exciton binding energy and band gap from which the absorption spectrum *without* Coulombic enhancement (αFree) can unambiguously be calculated without the need to invoke any further parameters. We have now added a sentence to make this more apparent.

Changes made:

On page 5:

Added after *[…by a factor ξ(E) beyond that expected for free electrons and holes (αC(E), red dashed line).]*

ξ(E) is the Coulomb enhancement factor derived from the values of the band gap and binding energy (see Equation 10 in the Supplementary Information) and is therefore not a free (independent) parameter of the model.

**• To what extent the recombination parameter k2 depends on the actual estimate of carrier concentration? Can realistic fluctuations in the carrier concentration improve agreement of extrapolated k2 with experiments?**

Author reply:

The charge-carrier concentration present during the transient spectroscopic measurements is not estimated, but well characterised from measurement of the excitation fluence used, and by taking into account the absorption depth profile and other parameters as detailed in the Supporting Information of the article describing the measurements. The fluctuations seen in the value of k2 derived from transient measurements are due to low signal to noise that is inherent to measurements, and in particular to optical pump terahertz probe spectroscopy which is a relatively new technique.

**• Is it possible to improve the statistics of transient spectroscopy measurements of figure 3 to better validate the conclusions of the paper and the actual value of the enhancement factor?**

Author reply:

The optical pump terahertz probe measurements (transient measurements) are extremely challenging given that they typically have very low signal to noise ratios and already require a double lock-in setup in order for any signal to be recordable. These measurements convey what is currently possible with state of the art technology; no other groups are able to obtain any better data. We are of course always working on ways to further improve this measurement technique, but at present, this presents the state of the art.