Peer Review File

Manuscript Title: Giant modulation of optical nonlinearity by Floquet engineering

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

The authors performed energy dependent optical pump and SHG probe experiments on MnPS3, and observed different dynamics when the pump photon energy is below 1 eV and at 2.2 eV. The former is below the resonant d-d transition with very fast dynamics, while the latter is around the transition with very slow dynamics. The authors use a Floquet theory to explain the data for pump below 1 eV. The result is quite interesting, but I have a few concerns at this stage.

1. MnPS3 has quite strong magneto-elastic coupling (For example, see Diana Vaclavkova et al 2D Mater. 7 035030. 2020). Why the suppression of the SHG can't be explained by light-induced lattice change, which results in the change of the magnetic SHG below T_N?

2. Usually, transient reflectivity change is around a few percent in pump-probe experiments. Using it as to exclude the Bloembergen-Pershan correction is not very convincing.

3. No data was shown for pump photon energy between 1 eV and 2.2 eV. Even if there might be two-photon absorption due to the d-d transition, it is probably very weak as it's a second order effect. What will the authors see if the pump is between 1 eV and 2.2 eV? It will be better to measure in this regime to compare. It might still be fast dynamics in this regime as the pump is still below the d-d transition. It will be interesting to investigate by both experiment and theory.

4. According to Fig. 2b, the most direct method to confirm the Floquet picture seems to measure the light-induced modulated gap. Can the authors measure transient absorption as in other 2D materials such as TMDCs?

5. The evidence of the c-type SHG is not very strong from the critical exponent. Just below T_N, there are only 3 or 4 data points for the fitting. At low temperature, the fitting doesn't seem very good compared with the neutron scattering experiments. For the regime just below T_N, can the authors measure with denser points?

I also have a few minor questions or comments.

6. The language of ABC stacking is confusing as it usually refer to trigonal structure. MnPS3 has monoclinic structure as it stacks by 1/3 of the lattice shift along one axis.

7. In the monoclinic structure, the b axis is perpendicular to the Mn-Mn bond. The mirror is perpendicular to the b axis. In the SHG polar pattern below 78K (Fig.1d), there are two mirrors in the data, perpendicular to the x and y axis. Is the x or y axis the b axis? Can the authors tell from SHG experiments?

8. In Fig. 4, e-g, the data has a peak ~180 deg, but the simulation has a peak away from it. What's the reason?

9. In the SI, what's the meaning of the characteristic energy scale epsilon_0 on page 6? Why is it so small?

10. The authors say that the experiment agrees well with theory in Fig. S8, but the discrepancy is

not small. Can the authors clarify it?

Referee #2 (Remarks to the Author):

The manuscript by Shan et al. demonstrates a significant modulation of non-linear optical properties (second harmonic generation, SHG) of a solid (MnPS3) through strong laser driving (Floquet engineering). Floquet engineering is one of the most promising protocols to non-thermally control the properties of solids. In spite of many interesting theoretical proposals, however, an experimental realisation is hampered by the typical runaway heating under strong driving. The system studied in the present manuscript seems to be an exception, where a modification nontrivial properties of the solid can be achieved with minimal heating. If the interpretation in correct, it would be an ideal realization of a Floquet engineering protocol, where a strong (almost 100%) modification of the optical properties is achieved, which reversibly follows the pump amplitude. Although the strongly ionic character of MnPS3 brings the setting somewhat close to a nonlinear manipulation of individual molecular units, I would view this paper as a landmark contribution to the out-of-equilibrium control of solids, which in my opinion definitely deserved publication in a high impact journal. I also find the presentation very clear, both in the main text and the supplement. I have the comments below:

** My first comment may be just semantics, but I nevertheless find it worthwhile to address here: Usually, Floquet engineering is interpreted such that the driving on some fast scale is use to generate a renormalised Hamiltonian, which then governs the dynamics on a much slower timescale. In the present case, there is at first sight no such timescale separation: The driving frequency is actually lower than the frequency omega of the SHG probe. One can still map this to Floquet engineering within the almost resonant subspace of the initial and final state of the SHG process, as worked out in the supplementary material, but I feel this aspect could be highlighted a bit more in the text. In fact, I find this twist of Floquet engineering, in which not some low energy Hamiltonian, but the intermediate steps of a scattering experiment are controlled by the periodic drive, novel in itself. It can probably be extended to other spectroscopies, such as Xray scattering. In this context, I would also ask what controls the validity of the Floquet description: As it is no longer the frequency separation between the drive and the SHG frequency omega, the validity should be related to the lifetime of the final state (Gamma_f)? What about the lifetime of the intermediate state?

** Another question refers to the theoretical analysis of the Floquet engineering of the nonlinear optical process: The driving field is coupled only to the transition between the driving between initial and final state. This leads to a mixing of these states, we well as a shift of their energies. One could also imagine also processes in which the intermediate state m is affected by the driving. I understand that the direct coupling i-m and f-m is weak, but since the effect of the driving is off resonant anyway, a dipole-allowed transition of the intermediate state m to any other state (such as a CT excitation of suitable symmetry, different form the symmetry of the state f) would renormalise the intermediate state and thus also affect the transition the SHG process. Can this be relevant? Or is it neglected because it would not affect the most relevant resonance E_i-E_f=2\omega?

** Although I agree that that the fact that the SHG follows the pump-probe cross-correlation is a strong support for the proposed off-resonant Floquet engineering, it seems that a much stronger proof for the proposed mechanism could be given if there would be a parameter regime in which the SHG can be enhanced rather than suppressed. Naively, it seems to me that this could be possible when the frequency omega is chosen such that un-driven process is further from resonance E_i-E_f=2\omega, and the Floquet engineering of the levels would bring it closer. In this case the state mixing “alpha” and the level shift could act in an opposite way on the SHG signal, giving a nontrivial frequency dependence of its relative change under driving to be analyzed.

** Although I find the quantitative theory experiment comparison in Fig 4c&d very compelling, I wonder whether there are ways to directly disentangle the effect of the Floquet level shift Delta E and the state mixing alpha. would it make sense to analyse the linear optical response in this respect: In discussion of Fig S4, authors say that the modification of Delta R/R is "likely also a result of Floquet engineering". Can one make this more explicit? Naively, it seems that the satte mixing alpha would be responsible to the bleaching (Delta R<0), and Delta E could give rise to a shift. Since the bleaching should be ~alpha^2 and the shift ~Delta E, where alpha and Delta E are linear in the field, can one use this to get an independent estimate of Delta E?

** The analysis around equation S11 neglects the Floquet sidebands, thus projecting the Floquet Hamiltonian to the resonant subspace of final and initial states. Again, I am wondering whether the effect of these sidebands, which are in fact a central to Floquet physics, could be activated by changing the frequency of the SHG probe. Naively, if the state i has an admixture of f offset by 2Omega, then there should be a resonant SHG process at E_f-E_i+Delta E=2(omega +/-Omega).

** The red solid line in Fig 3b is said to be the pump-probe cross correlation. In view of the nice theory-experiment comparison in Fig 4c and d, how would the theoretical prediction look in this plot?

Referee #3 (Remarks to the Author):

A. The manuscript by J-Y. Shan, et al reports the results of a pump probe optical experiment in the quasi-2D antiferromagnet MnPS3. This pump optical excitation causes the disappearance of the SHG signal only when the pump photon energy is non-resonant with an existing atomic-like transition. When the pump photon energy is higher, then the time-resolved dynamics are reminiscent of pump-induced heating. The authors model their observations using a Floquet-type hamiltonian which qualitatively reproduces well their results. The authors characterize this behavior as "Floquet engineering".
B. These results and interpretation are interesting and novel. They represent one more of the very few experimental example of Floquet materials (authors appropriately cite references [5] and [6]).
C. The data and approach are of high quality and there are no obvious deficiencies that invalidate the approach.
D. While the approach is valid, the authors do not discuss at all any uncertainty values. The authors should include uncertainties/error bars in their graphs. Also, are these results observed in more than 1 sample?
E. The conclusions are sound in the sense that the authors do eliminate some possible other explanations, and their chosen model is consistent with their data. I do, however, want to point out that the authors claim in a couple of places that their chosen model "quantitatively" agrees with their data. This is not the case as one can see very simply in figure 4, particularly in the pairs of panels c-d, e-f, and g-h. If the authors want to show quantitative agreement, they should make these pairs of graphs into a single graph overlapping the experimental data with the theoretical calculations. It is clear that the agreement is only qualitative not quantitative. This qualitative agreement between model and experiment is still strong evidence that "Floquet engineering" is occurring. However, this may mean that Nature is not the right journal (more on this below).
F. Here are some additional comments to consider in a subsequent version of this manuscript:
1) In the paragraph introducing the material MnPS3 (end of page 1) the authors mention the time-reversal odd second order susceptibility tensor. However, they don't justify why the time-reversal odd part is what is relevant for this material. This needs to be explained.
2) At the beginning of page 3, the authors mention that the energy of the pump photon is above 0.5 eV to avoid the tunneling ionization regime. This is a highly specialized term that needs to be explained, i.e. why is this regime most important for lower photon energies?
3) In the Methods section, the authors mention that the samples were characterized by energy dispersive x-ray spectroscopy and that the magnetization was measured using a SQUID

magnetometer. The authors should provided these data in the supplemental materials to assess the sample quality.
4) In supplemental S4 the authors say that they extracted the energy gap from previously reported data on this material but by different authors. Why wasn't this measurement done on the sample that they authors measured?

In the end I am not sure this manuscript meets this criterium for publication: "In general, to be acceptable, a paper should represent an advance in understanding likely to influence thinking in the field, with strong evidence for their conclusions." While the conclusions are supported by the data and model, I am not sure the paper is an "advance in understanding likely to influence the thinking in the field". I write this because this paper is an example (yes, one of the few) of a well identified approach of "Floquet engineering" in materials. The experiments are hard, and the effects are hard to detect (this is why there are so few experimental examples of it), but I do not think this particular paper will influence the thinking in the field.

Author Rebuttals to Initial Comments:

Referees' comments:

Referee #1 (Remarks to the Author):

The authors performed energy dependent optical pump and SHG probe experiments on MnPS3, and observed different dynamics when the pump photon energy is below 1 eV and at 2.2 eV. The former is below the resonant d-d transition with very fast dynamics, while the latter is around the transition with very slow dynamics. The authors use a Floquet theory to explain the data for pump below 1 eV. The result is quite interesting, but I have a few concerns at this stage.

1. MnPS3 has quite strong magneto-elastic coupling (For example, see Diana Vaclavkova et al 2D Mater. 7 035030. 2020). Why the suppression of the SHG can't be explained by light-induced lattice change, which results in the change of the magnetic SHG below T_N?

For the following reasons, we can rule out the possibility that the ultrafast suppression and recovery of magnetic SHG is due to a light-induced lattice change:

1. Sub-gap pumping can in principle induce transient lattice changes via several different mechanisms. Examples include (a) direct resonant excitation of phonons [e.g., Först *et al*., *Nat. Phys.* **7**, 854 (2011)], (b) resonant excitation of *d-d* transitions coupled to phonons [e.g., Sala *et al*., *PRB* **94**, 014430 (2016)], or (c) nonlinear absorption induced thermal expansion effects [e.g., Jackson Williams *et al*., *Sci. Rep.* **6**, 39506 (2016)]. However, in our experiments (Fig. 3b) the pump photon energy is far off-resonance from any phonon mode or *d-d* transition. Moreover, the observed effect is quite insensitive to photon energies below the *d-d* transition. Therefore, we can rule out mechanisms (a) or (b) being at play. Based on the fact that the SHG suppression is observed even using pump photon energies below 25 % of the band gap, and that the temporal profile of the magnetic SHG intensity is completely symmetric about time zero (Fig. 3b), we can also rule out nonlinear heating effects (c) playing any significant role.

2. Although $MnPS_3$ indeed has quite strong magneto-elastic coupling, the magnetic order parameter appears to be very robust against lattice distortions. Theoretical studies [Sivadas *et al*., *PRB* **91**, 235425 (2015)] estimate that a strain of several percent is required to change the magnetic order, and pressure dependence experiments show that the magnetic order is robust up to at least 1 GPa [Toyoshima *et al*., *J. Phys: Conf. Ser.* **150**, 042215 (2009)]. The large amplitudes of lattice distortion needed to suppress magnetic order are unlikely to be achieved using off-resonant excitation.

3. Even if the SHG could be suppressed via a light-induced lattice distortion, the distortion would have to be sustained on a timescale of order the inverse magnetic exchange energy (J^{-1}) in order to suppress the long-range magnetic order. Any subsequent recovery of the magnetic order

would also be limited by this timescale. However, J^{-1} is around 5 ps for $MnPS_3$ whereas we observe a suppression and recovery of SHG on the 0.1 ps timescale defined by the pulse duration. Therefore, the observed dynamics are too fast to be explained by magneto-elastic coupling induced effects.

We now include this information in paragraphs 4 and 9 of the main text.

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2. Usually, transient reflectivity change is around a few percent in pump-probe experiments. Using it to exclude the Bloembergen-Pershan correction is not very convincing.

The Bloembergen-Pershan correction relates the SHG susceptibility measured in reflection geometry $\chi_R^{(2)}$ to the intrinsic SHG susceptibility $\chi^{(2)}$ and is given by:

$$\frac{\chi_R^{(2)}}{\chi^{(2)}} = \left[\frac{2}{n(\omega)+1}\right]^2 \frac{1}{[n(2\omega)+n(\omega)][n(2\omega)+1]}$$

Based on our transient reflectivity measurements at both 1.55 eV and 3.1 eV photon energies, we can determine the pump induced changes in $n(\omega)$ and $n(2\omega)$ using the Fresnel equations. For the highest pump fluence used in our work, we find $\Delta n(\omega)/n(\omega) \approx -1.2$ % and $\Delta n(2\omega) \approx 0$, corresponding to a change in the Bloembergen-Pershan correction of +2.1 %. This is not only far too small to explain the over 90 % drop of the SHG intensity, but is also of opposite sign. Therefore, the observed SHG modulation must predominantly originate from changes to $\chi^{(2)}$. A detailed discussion of this point is now included in supplementary section S5.

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3. No data was shown for pump photon energy between 1 eV and 2.2 eV. Even if there might be two-photon absorption due to the d-d transition, it is probably very weak as it's a second order effect. What will the authors see if the pump is between 1 eV and 2.2 eV? It will be better to measure in this regime to compare. It might still be fast dynamics in this regime as the pump is still below the d-d transition. It will be interesting to investigate by both experiment and theory.

Following the Referee's suggestion, we performed time-resolved SHG measurements using both 1.3 eV and 1.55 eV pump photon energies. In both cases, the temporal profile and modulation amplitude of the SHG transients are similar to those acquired at lower photon energies. We have now included these new data in Fig. 3b. We have also extended our Floquet theory calculations into this higher pump photon energy regime and continue to find good agreement with the new data. This is now added to supplementary section S4.

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4. According to Fig. 2b, the most direct method to confirm the Floquet picture seems to measure the light-induced modulated gap. Can the authors measure transient absorption as in other 2D materials such as TMDCs?

We agree with the Referee that a direct method to confirm the Floquet picture is to measure the light-induced bandgap modulation. Unfortunately, transient absorption spectroscopy is difficult to apply to $MnPS_3$ for technical reasons – mainly it is challenging to generate a supercontinuum near 3 eV from 800 nm ultrafast pulses. Instead, we performed transient SHG spectroscopy, which is also sensitive to the electronic spectrum [see e.g., Fiebig *et al*., *PRL* **87**, 137202 (2001)] and can thus serve the same purpose.

We were able to acquire transient SHG spectra from 2.95 eV to 3.26 eV, which is near the detection edge of our CCD camera. In the un-driven case, the SHG intensity increases steeply near the band edge of $MnPS_3$ as expected. Upon sub-gap pumping, we observed that the band edge increases monotonically with pump fluence, in reasonable quantitative agreement with our theoretical predictions. We believe this is strong evidence supporting the Floquet picture. These new data have been added to Figs. 3e-g along with a discussion in the main text. Technical details of the transient SHG spectroscopy experiment have also been added to the Methods.

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5. The evidence of the c-type SHG is not very strong from the critical exponent. Just below T_N, there are only 3 or 4 data points for the fitting. At low temperature, the fitting doesn't seem very good compared with the neutron scattering experiments. For the regime just below T_N, can the authors measure with denser points?

Following the Referee's suggestion, we measured a much denser set of data points just below T_N from 72 K to 78 K. The critical exponent was re-fitted using these new data and now agrees even better with neutron scattering results within this temperature window. We emphasize that upon further cooling, our SHG data exhibits a crossover in the critical exponent, which is also consistent with neutron scattering results. These new data and fitting results are now included in Fig. 1d and in supplementary section S3.

I also have a few minor questions or comments.

6. The language of ABC stacking is confusing as it usually refers to trigonal structure. MnPS3 has monoclinic structure as it stacks by 1/3 of the lattice shift along one axis.

We agree with the Referee and have removed the language of “ABC stacking” throughout the main text and supplementary information.

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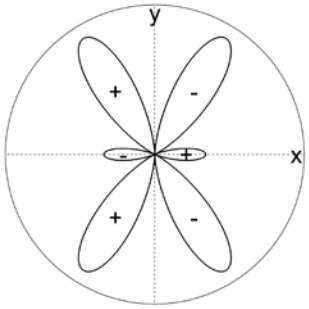
7. In the monoclinic structure, the b axis is perpendicular to the Mn-Mn bond. The mirror is perpendicular to the b axis. In the SHG polar pattern below 78K (Fig.1d), there are two mirrors in the data, perpendicular to the x and y axis. Is the x or y axis the b axis? Can the authors tell from SHG experiments?

In our convention, the b axis (y axis) is along the nearest-neighbor Mn-Mn bond and the mirror plane is perpendicular to the b axis. This convention is adopted from other works such as D. Vaclavkova *et al*., *2D Mater*. **7**, 035030 (2020) and K. Okuda *et al*., *J. Phys. Soc. Jpn*. **55**, 4456 (1986).

Although it may appear that there are two mirror planes in the SHG polar pattern, there is actually only one mirror plane (perpendicular to y). This is because the optical phase, which is not directly detected in an intensity measurement, alternates from one lobe to another as shown in the figure below. This allows us to unambiguously determine from the SHG polar pattern that the y axis is the b axis. We have now clarified this point in the caption of Fig. 1.



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8. In Fig. 4, e-g, the data has a peak ~180 deg, but the simulation has a peak away from it. What's the reason?

The data in Figures 4e & g actually do show peak positions offset slightly from 180°. This effect is most evident in the green and purples curves of Fig. 4e and the purple curve of Fig. 4g. The observed directions of these shifts are also consistent with our simulations in Figures 4f & h. The reason for this angular offset is subtle and is not directly relevant to the main conclusions of our

paper. Therefore, it was only briefly discussed in supplementary section S4 of the original submission. Following the Referee's question, we decided to expand this section to include a more detailed description. Below we provide a brief summary.

The angular (θ) anisotropy of the SHG intensity arises from two sources. The major source is the Rabi frequency anisotropy due to layer stacking, which produces an intensity peak at exactly 180°. The other source is related to the fact that the $|f\rangle$ state is actually a degenerate manifold of states – the excited sulfur hole and manganese electron can reside in different $3p$ and t_{2g} orbitals respectively. Upon driving, a different energy shift and mixing factor is induced between the $|i\rangle$ state and each of the different $|f\rangle$ states. Since these values all depend on the orientation of the driving field, this effect produces an additional modulation of the SHG intensity with θ, which serves to shift the intensity peak away from 180°.

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9. In the SI, what's the meaning of the characteristic energy scale epsilon_0 on page 6? Why is it so small?

The characteristic energy scale ϵ_0 is the ionization energy of the donor impurity, i.e., the energy necessary to move one electron from the donor level to the bottom of the conduction band. It is determined by the lattice dielectric permittivity and the effective mass of the conduction band. Our extracted value of ϵ_0 for $MnPS_3$ is 2.6 meV, which is a typical value for semiconductors. As a comparison, we reproduce a table from the textbook of Shklovskii & Efros, *Electronic properties of doped semiconductors*, showing values of ϵ_0 for conventional semiconductors. We have clarified this definition in supplementary section S2.

Table 1.1. Dielectric permittivities, effective masses, and theoretical and experimental values of the ground-state energy for selected semiconductors

Material	κ	$\frac{m}{m_0}$	E_{1s} (theor) [meV]	E_{1s} (expt) [meV]	
GaAs	12.5	0.066	5.67	Ge: 6.1; Se: 5.9; Sn: 5.9	Si: 5.8 S: 6.1
InP	12.6	0.08	6.8	7.28	
CdTe	10	0.1	13	13.8	

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10. The authors say that the experiment agrees well with theory in Fig. S8, but the discrepancy is not small. Can the authors clarify it?

We apologize if our language was misleading. The intention was simply to point out that the general trend of the experimental and theoretical curves agree. Namely, both curves show a drop in SHG intensity that increases monotonically with drive amplitude, saturating to –100 % near the same critical drive amplitude. The theoretical curve is based on an extremely simplistic model that assumes a uniformly heated cylinder of material, which neglects spatial gradients of the pump and probe beams, heat diffusion and thermally induced structural changes. Therefore, we do not expect, nor do we mean to claim, that the theoretical curve provides a good quantitative fit to the experimental data. We have clarified this point in supplementary section S7 and also added error bars to the figure (now Fig. S9).

We thank the Referee for the many helpful suggestions to improve our manuscript.

Referee #2 (Remarks to the Author):

The manuscript by Shan et al. demonstrates a significant modulation of non-linear optical properties (second harmonic generation, SHG) of a solid (MnPS3) through strong laser driving (Floquet engineering). Floquet engineering is one of the most promising protocols to non-thermally control the properties of solids. In spite of many interesting theoretical proposals, however, an experimental realisation is hampered by the typical runaway heating under strong driving. The system studied in the present manuscript seems to be an exception, where a modification nontrivial properties of the solid can be achieved with minimal heating. If the interpretation in correct, it would be an ideal realization of a Floquet engineering protocol, where a strong (almost 100%) modification of the optical properties is achieved, which reversibly follows the pump amplitude. Although the strongly ionic character of MnPS3 brings the setting somewhat close to a nonlinear manipulation of individual
molecular units, I would view this paper as a landmark contribution to the out-of-equilibrium control of solids, which in my opinion definitely deserved publication in a high impact journal. I also find the presentation very clear, both in the main text and the supplement. I have the comments below:

** My first comment may be just semantics, but I nevertheless find it worthwhile to address here: Usually, Floquet engineering is interpreted such that the driving on some fast scale is use to generate a renormalised Hamiltonian, which then governs the dynamics on a much slower timescale. In the present case, there is at first sight no such timescale separation: The driving frequency is actually lower than the frequency omega of the SHG probe. One can still map this to Floquet engineering within the almost resonant subspace of the initial and final state of the SHG process, as worked out in the supplementary material, but I feel this aspect could be highlighted a bit more in the text. In fact, I find this twist of Floquet engineering, in which not some low energy Hamiltonian, but the intermediate steps of a scattering experiment are controlled by the periodic drive, novel in itself. It can probably be extended to other spectroscopies, such as Xray scattering. In this context, I would also ask what controls the validity of the Floquet description: As it is no longer the frequency separation between the drive and the SHG frequency omega, the validity should be related to the lifetime of the final state (Gamma_f)? What about the lifetime of the intermediate state?

We agree with the Referee that there is no renormalized many-body Hamiltonian in our case since we are dealing with single-ion states. Nevertheless, there still exists a notion of timescale separation. The fast timescale (~ 5 fs) is the driving period whereas the slow timescale (~ 100 fs) is the pulse width, which sets the timescale over which the shift ΔE and the mixing α vary (see main text Fig. 2). The fast oscillating drive induces a quasi-static change in the time-averaged optical transition amplitudes within the subspace of $|i\rangle$ and $|f\rangle$, causing the SHG modulation to

follow the slow timescale of the pulse envelope. As suggested by the Referee, we have now highlighted this aspect in paragraph 8 of the main text.

In order for our Floquet description using $|i\rangle$ and $|f\rangle$ as pure states to be valid (main text Eqn. 3), the lifetime of these states must be sufficiently long. Otherwise, one must use density matrices to express the states, and our analysis would be invalid. It has been shown (see e.g., Berman & Malinovsky, *Principles of laser spectroscopy and quantum optics*, p.66) that in the limit $\gamma_f \ll \Omega^R$, where Ω^R is the Rabi frequency, the off-diagonal elements in the density matrices can be neglected and analysis using pure states is valid. In our case, γ_f is around 30 meV and Ω^R is an order of magnitude larger. Therefore, our Floquet picture is valid. We do not consider the intermediate state lifetime because it is not a relevant state in this Floquet problem. We have now made this point clearly in supplementary section S4.

** Another question refers to the theoretical analysis of the Floquet engineering of the nonlinear optical process: The driving field is coupled only to the transition between the driving between initial and final state. This leads to a mixing of these states, as well as a shift of their energies. One could also imagine processes in which the intermediate state m is affected by the driving. I understand that the direct coupling i-m and f-m is weak, but since the effect of the driving is off resonant anyway, a dipole-allowed transition of the intermediate state m to any other state (such as a CT excitation of suitable symmetry, different form the symmetry of the state f) would renormalise the intermediate state and thus also affect the transition the SHG process. Can this be relevant? Or is it neglected because it would not affect the most relevant resonance E_i-E_f=2\omega?

We agree with the Referee that it is possible for the $|m\rangle$ state to couple to another state with suitable symmetry, such as a two-electron charge-transfer state. However, since that state would lie at even higher energies, which is even more off-resonant from our drive, the Floquet modulation of the $|m\rangle$ state will not play a dominant role in this problem. As the Referee rightly points out, another major reason why we do not consider the $|m\rangle$ state modulation is that even if its energy is shifted by the drive, it would have negligible effect on the resonant SHG intensity at energy $E_i - E_f$. Quantitatively, we find that even if the $|m\rangle$ state is hypothetically shifted down by an amount $\Delta E_{max} \approx 100$ meV as is the case for $|i\rangle$, it would only slightly change $\Delta I^{mag}/I^{mag}$ from –91 % to –88 %. We have now added this discussion to supplementary section S4.

** Although I agree that that the fact that the SHG follows the pump-probe cross-correlation is a strong support for the proposed off-resonant Floquet engineering, it seems that a much stronger

proof for the proposed mechanism could be given if there would be a parameter regime in which the SHG can be enhanced rather than suppressed. Naively, it seems to me that this could be possible when the frequency omega is chosen such that un-driven process is further from resonance E_i-E_f=2\omega, and the Floquet engineering of the levels would bring it closer. In this case the state mixing "alpha" and the level shift could act in an opposite way on the SHG signal, giving a nontrivial frequency dependence of its relative change under driving to be analyzed.

The Referee's suggestion would certainly work if $|i\rangle$ and $|f\rangle$ were true atomic states. However, in reality $|i\rangle$ and $|f\rangle$ are states at the edge of a dispersive band. This means that the line shape of the SHG spectrum is not a Lorentzian centered at $2\hbar\omega = E_i - E_f$, but rather that of an absorption edge with a characteristic upturn at $2\hbar\omega = E_i - E_f$. Thus, even if the SHG energy were tuned slightly above $E_i - E_f$, one would still expect to see suppression rather than enhancement of the SHG signal upon pump-induced bandgap widening.

To verify this picture, we performed time-resolved SHG spectroscopy measurements on $MnPS_3$ over an SHG energy range from 2.95 eV to 3.26 eV. As expected, in the un-pumped case, the SHG intensity increases monotonically with probe photon energy above the band gap. Upon sub-gap pumping, we observed the band gap to increase monotonically with pump fluence, in reasonable quantitative agreement with our theoretical predictions. This supports our previous claim that the SHG intensity is transiently suppressed over the entire SHG energy range. Although we do not rule out the possibility of observing a transiently enhanced SHG signal at even higher photon energies (3.26 eV is at the detection edge of our CCD camera), we believe these new results already provide strong evidence supporting the Floquet engineering picture. These new data have been added to Figs. 3e-g along with a discussion in the main text. Technical details of the transient SHG spectroscopy experiment have also been added to the Methods.

** Although I find the quantitative theory experiment comparison in Fig 4c&d very compelling, I wonder whether there are ways to directly disentangle the effect of the Floquet level shift Delta E and the state mixing alpha. would it make sense to analyse the linear optical response in this respect: In discussion of Fig S4, authors say that the modification of Delta R/R is "likely also a result of Floquet engineering". Can one make this more explicit? Naively, it seems that the satte mixing alpha would be responsible to the bleaching (Delta R<0), and Delta E could give rise to a shift. Since the bleaching should be ~alpha^2 and the shift ~Delta E, where alpha and Delta E are linear in the field, can one use this to get an independent estimate of Delta E?

Our new transient SHG spectroscopy data (see response to previous comment) allow us to directly measure the level shift and thus disentangle it from state mixing effects. The observed level shift is consistent with our theoretical predictions.

Following the Referee's suggestion, we also explored the possibility of disentangling the level shift and mixing effects via the linear reflectivity. The quantum mechanical expression for the linear electric susceptibility is:

$$\chi_{ij} \sim \frac{\langle i|r_i|f\rangle\langle f|r_j|i\rangle}{E_f - E_i - \hbar\omega}$$

Under Floquet driving conditions, E_i shifts down by ΔE and the state $|i\rangle$ gains a mixing factor $\cos\alpha$. The refractive index n can be computed from χ using the relation $n^2 = \varepsilon = 1 + \chi$, where ε is the relative permittivity. The linear reflectivity R can then be obtained from the refractive index n through the Fresnel formula. For small driving amplitudes, we show that to lowest order:

$$\frac{\Delta R}{R} \propto -\left(\frac{1}{2}\alpha^2 + \frac{\Delta E}{E_f - E_i - \hbar\omega}\right)$$

Since $\alpha \propto E^{pu}$ and $\Delta E \propto (E^{pu})^2$, both the state mixing and level shift contributions to the differential reflectivity are quadratic in E^{pu} . Upon expanding to higher orders, both state mixing and level shift continue to contribute terms of equal order in E^{pu} . Therefore, this approach does not allow us to disentangle the effects of level shift and state mixing. We have added this discussion to supplementary section S5.

** The analysis around equation S11 neglects the Floquet sidebands, thus projecting the Floquet Hamiltonian to the resonant subspace of final and initial states. Again, I am wondering whether the effect of these sidebands, which are in fact central to Floquet physics, could be activated by changing the frequency of the SHG probe. Naively, if the state i has an admixture of f offset by 2Omega, then there should be a resonant SHG process at E_f-E_i+Delta E=2(omega +/-Omega).

The time-averaged wavefunction amplitude of the n^{th} order Floquet sideband is approximately $[\hbar\Omega^R/(E_f - E_i)]^{|n|}$. The lowest-order resonance involving the sidebands occurs at $2\hbar\omega = E_{f'} - E_{i'} \pm 2\hbar\Omega$ due to parity selection rules. Since the sideband wavefunction appears in $\chi_{ijk}^{ED(c)}$ twice (Eqn. 1 of the main text), the magnitude of $\chi_{ijk}^{ED(c)}$ at the $2\hbar\omega = E_{f'} - E_{i'} \pm 2\hbar\Omega$ resonances is weaker than the main resonance at $2\hbar\omega = E_{f'} - E_{i'}$ by a factor of

$[\hbar\Omega^R/(E_f - E_i)]^4$. For $E_{\max}^{pu} = 10^9$ V/m, the resonances due to the Floquet sidebands would be weaker than the main resonance by a factor 10^{-4}, which unfortunately cannot be experimentally resolved. We have now included this discussion along with a calculation of sideband resonance in supplementary section S4.

** The red solid line in Fig 3b is said to be the pump-probe cross correlation. In view of the nice theory-experiment comparison in Fig 4c and d, how would the theoretical prediction look in this plot?

Following the Referee's suggestion, we plot in Fig. 3b the theoretical prediction, which is a convolution between the probe pulse profile and the predicted temporal SHG profile caused exclusively by the pump pulse. This curve is slightly broader than the pump-probe cross correlation, but still agrees very well with our experimental data. We have now replaced the cross-correlation curve with this theoretical prediction in Fig. 3b and provided an explanation in paragraph 9 of the main text.

We thank the Referee for the many suggestions that have helped to improve our manuscript.

Referee #3 (Remarks to the Author):

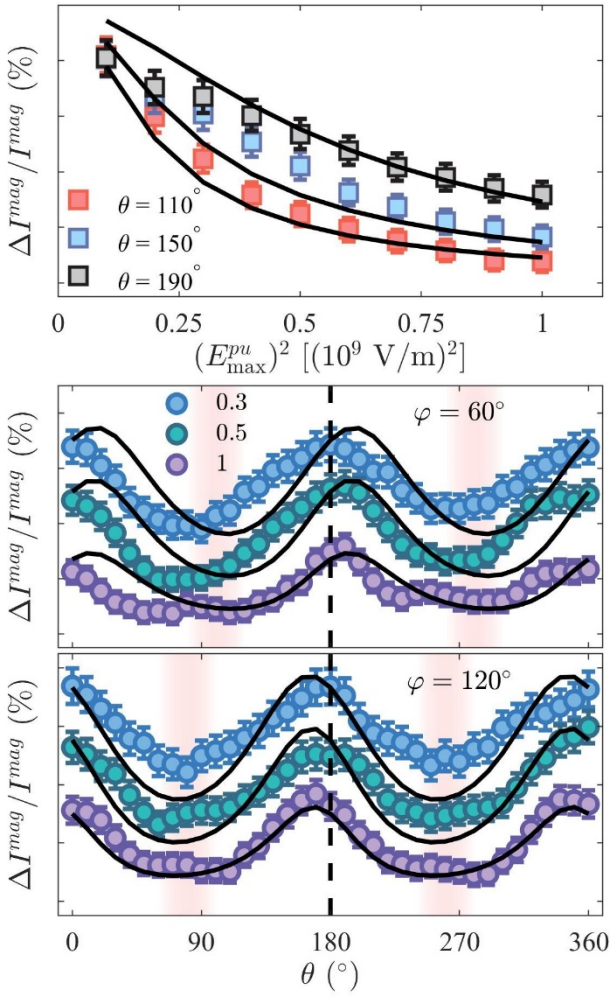
A. The manuscript by J-Y. Shan, et al reports the results of a pump probe optical experiment in the quasi-2D antiferromagnet MnPS3. This pump optical excitation causes the disappearance of the SHG signal only when the pump photon energy is non-resonant with an existing atomic-like transition. When the pump photon energy is higher, then the time-resolved dynamics are reminiscent of pump-induced heating. The authors model their observations using a Floquet-type hamiltonian which qualitatively reproduces well their results. The authors characterize this behavior as "Floquet engineering".
B. These results and interpretation are interesting and novel. They represent one more of the very few experimental examples of Floquet materials (authors appropriately cite references [5] and [6]).
C. The data and approach are of high quality and there are no obvious deficiencies that invalidate the approach.
D. While the approach is valid, the authors do not discuss at all any uncertainty values. The authors should include uncertainties/error bars in their graphs. Also, are these results observed in more than 1 sample?

We have now added error bars to all the SHG data, which represent the standard error of the mean over several independent measurements. These results were reproduced in two samples from two different growth batches. We have now included this information in the figure captions and the Methods section.

E. The conclusions are sound in the sense that the authors do eliminate some possible other explanations, and their chosen model is consistent with their data. I do, however, want to point out that the authors claim in a couple of places that their chosen model "quantitatively" agrees with their data. This is not the case as one can see very simply in figure 4, particularly in the pairs of panels c-d, e-f, and g-h. If the authors want to show quantitative agreement, they should make these pairs of graphs into a single graph overlapping the experimental data with the theoretical calculations. It is clear that the agreement is only qualitative not quantitative. This qualitative agreement between model and experiment is still strong evidence that "Floquet engineering" is occurring. However, this may mean that Nature is not the right journal (more on this below).

Below we replot the results from Figures 4c-d, e-f, and g-h with the theoretical calculations (lines) and experimental data (markers) overlaid on the same graph. Both the trend and the absolute SHG modulation amplitude agree quite well with no free parameters, which is why we had previously claimed quantitative agreement. However, we understand the Referee’s concern

that there remain some deviations between theory and experiment. Therefore, we have removed our use of the word “quantitative”.



To further strengthen our claim that Floquet engineering is occurring, we have now directly measured the light-induced bandgap modulation by performing transient SHG spectroscopy measurements. We were able to acquire transient SHG spectra from 2.95 eV to 3.26 eV, which is near the detection edge of our CCD camera. In the un-driven case, the SHG intensity increases steeply near the band edge of $MnPS_3$ as expected. Upon sub-gap pumping, we observed the band edge to increase monotonically with pump fluence, in reasonable quantitative agreement with our theoretical predictions. These new data have been added to Figs. 3e-g along with a discussion in the main text. Technical details of the transient SHG spectroscopy experiment have also been added to the Methods.

F. Here are some additional comments to consider in a subsequent version of this manuscript:

1) In the paragraph introducing the material MnPS3 (end of page 1) the authors mention the time-reversal odd second order susceptibility tensor. However, they don't justify why the time-reversal odd part is what is relevant for this material. This needs to be explained.

Above T_N the system is inversion symmetric, so the bulk second-order electric-dipole susceptibility tensor χ^{ED} vanishes. Below T_N, the AFM order breaks the inversion symmetry of the underlying lattice, allowing a finite χ^{ED}. It is empirically shown that the measured χ^{ED} couples linearly to the AFM order parameter. This means that χ^{ED} switches sign under time-reversal (i.e., under sign reversal of the order parameter), satisfying the definition of a time-reversal odd (c-type) tensor. In principle, a time-reversal even (i-type) χ^{ED} can also exist, but this is not experimentally detected. We have now added a sentence in paragraph 5 of the main text to clarify this point.

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2) At the beginning of page 3, the authors mention that the energy of the pump photon is above 0.5 eV to avoid the tunneling ionization regime. This is a highly specialized term that needs to be explained, i.e. why is this regime most important for lower photon energies?

We apologize for not being clear on this point. We avoided lower pump photon energies for two main reasons. First, at low frequencies, quantum tunneling between the valence and conduction band – which are tilted by the applied electric field – is enhanced, leading to the possibility of dielectric breakdown. Indeed, there have been several reports of intense low-frequency (THz scale) drive induced insulator-to-metal transitions [e.g., Yamakawa *et al*., *Nat. Mater.* **16**, 1100 (2017); Liu *et al*., *Nature* **487**, 345 (2012)]. Second, as discussed in supplementary section S8, photo-assisted virtual hopping leads to a renormalization of the bandwidth. The renormalization factor – determined by the Floquet parameter $eaE^{pu}/\hbar\Omega$ – is enhanced at low frequencies, which can make it more challenging to isolate the single-ion effects discussed in the manuscript. We have now made these points more clearly in paragraph 9 of the main text.

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3) In the Methods section, the authors mention that the samples were characterized by energy dispersive x-ray spectroscopy and that the magnetization was measured using a SQUID magnetometer. The authors should provide these data in the supplemental materials to assess the sample quality.

We have now included all of these data in supplementary section S9.

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4) In supplemental S4 the authors say that they extracted the energy gap from previously reported data on this material but by different authors. Why wasn't this measurement done on the sample that the authors measured?

Following the Referee's suggestion, we measured the absorption spectrum of the sample that the SHG measurements were collected on. The energy gap extracted from this new dataset is 3.09 ± 0.04 eV, which is similar to the gap extracted from previously reported data. We have now replaced the data and analysis in supplementary section S2 with these new results.

In the end I am not sure this manuscript meets this criterion for publication: "In general, to be acceptable, a paper should represent an advance in understanding likely to influence thinking in the field, with strong evidence for their conclusions." While the conclusions are supported by the data and model, I am not sure the paper is an "advance in understanding likely to influence the thinking in the field". I write this because this paper is an example (yes, one of the few) of a well identified approach of "Floquet engineering" in materials. The experiments are hard, and the effects are hard to detect (this is why there are so few experimental examples of it), but I do not think this particular paper will influence the thinking in the field.

We thank the Referee for the positive comments about our work and for the many helpful suggestions to improve our manuscript. However, we respectfully disagree with their assessment of its potential impact. In addition to demonstrating a novel pathway to coherently engineer the optical properties of a material *in situ*, we believe that our work will influence thinking in the field of condensed matter physics in two major ways.

First, despite the large number of theoretical proposals for Floquet engineering in quantum materials that have emerged in recent years, there is a dearth of experiments. It is generally believed that runaway heating is inevitable under the requisite strong driving conditions, dimming prospects for experimentally realizing Floquet engineering. Our work completely overturns this viewpoint by demonstrating a novel strategy to achieve giant Floquet engineering effects without any measurable heating. This strategy can be applied broadly to gapped materials and is anticipated to accelerate progress in Floquet engineering research, particularly on the experimental front.

Second, much theoretical work on Floquet engineering to date has focused on photo-assisted hopping between neighboring ions as a means to control electronic and magnetic properties. On the other hand, the effects of periodic driving at the local single-ion level have largely been overlooked. Our work shows that under strong driving conditions, electronic structure changes

induced by single-ion effects can be very large and can dominate over inter-site effects. Furthermore, our work shows that these effects can be accurately predicted in a materials specific way using Floquet theory calculations on single-ion models. Therefore, we anticipate our work to open new lines of investigation into the use of single-ion level Floquet engineering to control the electronic and magnetic properties of targeted materials, and to potentially realize new out-of-equilibrium phases of matter.

For all of these reasons, we believe our work will influence thinking in this field.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

The authors addressed most of my comments in the revision. I am not sure the transient SHG measures the band gap as the selection rule for SHG is different from linear absorption. In Fiebig et al., PRL 87, 137202 (2001),which the authors mentioned in the reply, the sharp peaks associated with different crystal field/spin orbit transitions have double the energy in SHG than that in the linear absorption. See Fig. 1. Even though the Floquet engineering is not the common one with renormalized Hamiltonian that the community usually talks about, the non-thermal path way demonstrated in this work is very interesting. Frankly speaking, I did not realize it until I read referee 2's report. The terminology here is a bit misleading in this regard, which gives me a bit of mixed feeling. I would certain recommend this work to be published in Nature Physics. I think I am also fine for this work to be published in Nature.

Referee #2 (Remarks to the Author):

The authors have provided a conclusive reply to all my questions. The revised manuscript now convincingly demonstrates Floquet engineering in MnPS3. It is one of the very few experiments in this field, in spite of an abundance of theoretical proposals. In addition, the control of the inter-atomic transitions demonstrated here is conceptually different from previous experimental demonstrations of Floquet engineering in solids (Refs 5 and 6), which are based on band structure engineering. I recommend publication of this manuscript in Nature.

Referee #3 (Remarks to the Author):

I appreciate the authors replies to all the referees's comments. I have only one more issue that I think it's important. The data presented in figure 4 is, however, still presented misleadingly. To show the best comparison between their model and experiment the calculation results should be plotted together with the experimental data, as the authors did in the reply to referees. While this could be seen as a matter of style, it really is not since it makes it harder for the reader to assess the validity of the theoretical model and explanation of the results.
I urge the authors to make this change.

Author Rebuttals to First Revision:

Referee #1 (Remarks to the Author):

The authors addressed most of my comments in the revision. I am not sure the transient SHG measures the band gap as the selection rule for SHG is different from linear absorption. In Fiebig et al., PRL 87, 137202 (2001), which the authors mentioned in the reply, the sharp peaks associated with different crystal field/spin orbit transitions have double the energy in SHG than that in the linear absorption. See Fig. 1.

In general, an SHG spectrum will exhibit a peak when either the fundamental photon energy or the SHG photon energy is resonant with an optical transition. In the former case, a peak in the linear absorption spectrum results in a peak at twice the energy in the SHG spectrum. In

the latter case, a peak in the linear absorption spectrum results in a peak at the same energy in the SHG spectrum. The sharp peaks reported by Fiebig *et al*. are due to the former. In contrast, the feature we report in $MnPS_3$ is due to the latter, which is expected because the absorption spectrum of $MnPS_3$ is completely featureless over the range of fundamental photon energies we use. We have now added a sentence to paragraph 11 of the main text to clarify this point.

Even though the Floquet engineering is not the common one with renormalized Hamiltonian that the community usually talks about, the non-thermal path way demonstrated in this work is very interesting. Frankly speaking, I did not realize it until I read referee 2's report. The terminology here is a bit misleading in this regard, which gives me a bit of mixed feeling. I would certain recommend this work to be published in Nature Physics. I think I am also fine for this work to be published in Nature.

In paragraph 7 of the main text, we have now added a brief discussion to more clearly differentiate the two types of Floquet engineering.

Referee #3 (Remarks to the Author):

I appreciate the authors replies to all the referees's comments. I have only one more issue that I think it's important. The data presented in figure 4 is, however, still presented misleadingly. To show the best comparison between their model and experiment the calculation results should be plotted together with the experimental data, as the authors did in the reply to referees. While this could be seen as a matter of style, it really is not since it makes it harder for the reader to assess the validity of the theoretical model and explanation of the results. I urge the authors to make this change.

We have changed Fig. 4 of the main text according to the Referee’s advice.
