nature portfolio

Peer Review File

Visualization and Quantum Control of Light-Accelerated Condensates by Terahertz Multi-dimensional Coherent Spectroscopy

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In this work, the authors have used a well-developed 2-D spectroscopy method to study coherent evolution of two superconducting excitations. They show that more information can be gained when the pump and probe light-pulses have significant overlap in time. This finding is not a new finding and has been seen previously in the optical frequency regime.
The paper is full of abbreviations which makes it difficult to read. Several important quantities, for example SC order parameter and Higgs frequency, etc., are not defined until the theory section. In the present form, it is difficult to follow the work. It is not clear which two SC excitations are being probed.

In the Methods, it is shown that the SC order-parameter can be expressed in terms of one of the four PS components. Can the authors comment on the physical interpretation of these components and clarify why only one specific component is related to the order-parameter and why electric current in Eq. (9) is related to the zeroth component? Are they related to the spin-spin correlations?

It is mentioned that Eq. (6) is for homogenous system without justifying its use or giving any idea how it is obtained.

The results reported in the manuscript may be correct but the presentation is too convoluted to follow. I do not recommend this work in its present form for publication.

Reviewer #2 (Remarks to the Author):

In the paper entitled "Visualization and Light-Driven Entanglement of Quantum Systems using Terahertz Multi-Dimensional Coherent Spectroscopy" by Martin Mootz, Liang Luo, Jigang Wang, and Ilias E. Perakis, the authors simulate Multi-Dimensional Coherent THz spectroscopy experiments.
In particular, they use two phase-locked THz laser pulses to gain super-resolution visualization of non-equilibrium quantum states with dissipationless current flow coherently controlled via relative phase accumulation of two correlated excitations.
They analyze the possibility of phase dependent tuning of photogenerated nonlinear interactions between SC excitations. In particular, they demonstrate the coherent steering of a superconducting state into tunable accelerated condensate states with THz inversion symmetry breaking during light-wave oscillation cycles.
Above a critical driving, they find Correlated-Wave-Mixing and inversion-symmetry-breaking Wave Mixing peaks together with more conventional ones and consider these a possible way in the related experiment to detect the a THz-time-periodically-driven superconducting state. Moreover, they characterize these unconventional peaks and determine their source terms in the equations.

These results are definitely novel and of interest to the community studying out-of-equilibrium superconductivity, but also to the wider community of researchers involved in (i) the characterization of the out-of-equilibrium response of and (ii) the optical control of unconventional materials.

The references provided are adequate in number and span the proper portion of existing literature.

The developed quantum kinetic modeling is very convincing and fully supports the drawn conclusions. Its comprehensiveness will definitely influence the field and set a new standard.

I consider sufficient the level of detail provided in the main text and in the supplementary materials, together with the related references cited, to allow a researcher to reproduce the calculations.

Accordingly, I do consider this paper acceptable for publication in Communications Physics in its current form.

Reviewer #3 (Remarks to the Author):

In their manuscript "Visualization and Light-Driven Entanglement of Quantum systems Using Terahertz Multi-Dimensional Coherent Spectroscopy," Martin Mootz and co-authors present a theoretical study of the types of things that it might be possible to see by applying Multi-Dimensional Coherent THz (MDC-THz) experiments to superconductors. The authors claim to be able to predict "experimental signatures of a THz-time-periodically-driven non-equilibrium [superconducting] state."

The extension of multi-dimensional coherent spectroscopy techniques into the terahertz regime is a hot topic in ultrafast spectroscopy, with several different groups currently pursuing experiments of this sort. In order for these experiments to be able to be guided and interpreted, it is important to have a firm understanding of the spectroscopy technique's theoretical underpinnings, and so the topic presented by the authors is very welcome. Beyond this, recent studies into the possibility of using ultrafast pulses to induce superconductivity in different types of systems heightens the potential importance of this manuscript.

Having noted these facts, however, the paper suffers from a severe lack of clarity to the point where I can barely understand at many points what the authors are trying to say. For example, the introductory paragraph is uncomfortably dense and jargon-heavy. There are excessive amounts of acronyms (SC, IS, CWM, ISWM, PP, FWM, HHG); there are far too many highly specialized terms for an introductory paragraph. Following the first paragraph, the language gets more plainspoken—which is welcome—but major sources of confusion remain. To pick on just one or two sentences: At the top of p. 3 the authors write that "one can steer the system into either [quasi-particle] or gapless-[superconducting] long-living such states…" I don't think it is possible to steer a system into a quasiparticle, nor do I understand from this phrasing what the authors are really trying to describe. Below this, the authors write that "…collective modes of [superconducting] states do not couple linearly to electromagnetic fields without finite Cooper-pair momentum. The latter can be induced…" It is not clear from this sentence whether "the latter" refers to "electromagnetic fields" or "finite Cooper-pair momentum."

Given the issues of confusion that I am left with after reading this manuscript, I unfortunately cannot recommend publication.

Visualization and Quantum Control of Light-Accelerated Condensates by Terahertz Multi-dimensional Coherent Spectroscopy by Martin Mootz, Liang Luo, Jigang Wang, and llias E. Perakis

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Report of Reviewer #1

In this work, the authors have used a well-developed 2-D spectroscopy method to study coherent evolution of two superconducting excitations. They show that more information can be gained when the pump and probe light-pulses have significant overlap in time. This finding is not a new finding and has been seen previously in the optical frequency regime.

Our response (#1): We appreciate the referee's careful reading of our manuscript. We agree with the referee that, in semiconductors and other previously studied systems, it is known that new signals are generated when pump and probe pulses overlap in time. Our original manuscript included some of these references in semiconductors with rigid energy bandgap, where four-wave-mixing and Raman signals coming from interference between pump and probe excitations are well known. In superconductors, theoretical studies so far mostly did not study the role of interference between pump and probe. Many works consider a single pulse or calculate pump-probe responses when the probe comes after the pump. Raman responses have been discussed and are included in our theory. However, the seventh-order and higher non-perturbative responses coming from pump-probe excitation quantum interference lead to new 2D THz spectral peaks distinct from pump-probe, four-wave-mixing, and high-harmonic generation peaks studied before, with unique temperature and electric field dependencies that differ from those of the known pump-probe, four-wave-mixing and high-harmonic generation signals. We are sorry for any misunderstandings leading to the statement that "This finding is not a new finding and has been seen previously in the optical frequency regime." Referee 2 also clearly summarizes our new results discussed for the first time here and how they differ from previous results. We have substantially edited the manuscript to make sure that there are no misunderstandings. Furthermore, the edited Supplementary Information presents a very detailed derivation and discussion that now more clearly points out what terms are new and which terms recover previous results. Our presented results address the 2D THz response of a superconducting quantum system, whose energy gap arises from electronic pairing correlations and not by the bandstructure as in previous semiconductor 2D spectroscopy studies. They are clearly distinct from previous experimental and theoretical 2D spectroscopy results, which are recovered by some of the terms in our full gauge invariant theory that are pointed out in the Supplementary Information.

We summarize below several points that distinguish our work from prior works and also refer to the clear summary by referee 2 of our new results and how they differ from previous ones:

(1) Clarifications on our quantum kinetic simulations and their difference from conventional Anderson pseudo-spin models: Ultrafast coherent nonlinear spectroscopy experiments have been mostly analyzed, so far, by using theories based on Liouville and Bloch equations, or nonlinear and Raman perturbative susceptibilities/response functions, which generalize corresponding approaches developed for understanding the femtosecond coherent nonlinear response in semiconductor quantum wells starting in the 1980's. In undoped semiconductors and other previously studied systems, the energy gap is mainly determined by the bandstructure, and a rigid band approximation is a good starting point. In quantum materials, our own work and others have pointed out the importance of considering "soft bands" modified by the optical excitation beyond simple screening effects: the predicted transition in 2D THz spectral lineshape above critical pump driving does not occur otherwise. In superconductors considered here, the energy gap arises from off-diagonal long-range order and order parameter. Our previous theoretical results referenced in the manuscript show how previous experiments must be interpreted in terms of a long-lived gapless superconductivity moving condensate state driven nonlinearly by tuning multi-cycle THz pulses. This light-induced non-equilibrium condensate state is characterized by a finite order parameter but zero quasi-particle energy gap. We have discussed elsewhere the existence of three long-lived (100's ps) regimes after the pulse, which are controlled nonthermally by tuning multi-cycle THz pulses: quasiparticle prethermalized states, quenched superconducting states, and gapless superconductivity. The clear experimental evidence not seen in previously studied systems, including superconductors with significant disorder, led us to develop the theory presented here. Our quantum kinetic simulations and their difference from conventional Anderson pseudo-spin models or perturbative Raman coherent effects suggest that the experimentally observed anomalous temperature and electric field dependencies observed in our experiments can be elucidated by using 2D THz spectroscopy. This paper demonstrates that this is the case. We believe that this significant new result, nicely summarized by referee 2, warrants publication in Communications Physics.

As we have discussed in the revised manuscript and in the figures, previous known 2D THz or optical 2D spectroscopy results agree with our calculation if we neglect the pump-probe superconducting off-diagonal order parameter modulation controlled by the relative phase accumulation between pump and probe fields, which parametrically drives the Anderson pseudo-spin oscillators. This is a non-perturbative way that contributes to seventh order or higher responses not discussed before, which dominate above critical driving over previously discussed third or fifth order Raman responses. In the case of superconductors, the persisting light-induced Cooper pair center-of-mass momentum photogenerated nonlinearly when electromagnetic propagation is included in our calculation, and the light-wave acceleration of the BCS ground state into a Cooper-pair moving condensate state with oscillating momentum change the *entire* BCS state in a non-perturbative way. As discussed in detail in the Supplementary Information, such *nonlinear quantum transport* light-induced effects and gapless superfluid states predicted by our theory, arising from THz-time-periodic nonlinear ultrafast driving, have been verified experimentally, both in clean A15 BCS superconductors and in high temperature iron pnictide superconductors, and are *in addition* to the previously studied Anderson pseudospin and Raman nonlinearities. We have already discussed these important points and differences from other works in our prior publications referenced in the manuscript. The 2D THz spectra discussed for the first time here allow super-resolution ultrafast imaging that clearly reveals behaviors and light-induced correlations which differ from previously studied simple BCS or weakly interacting multi-band superconductors such as MgB2.

To summarize, we have already established that light-wave acceleration of oscillating center-of-mass condensate motion can lead to light-induced gapless superconductivity and forbidden modes. Recent experimental observations of high harmonic generation at equilibrium-symmetry forbidden frequencies, followed by a long-lived (100's ps) gapless non-equilibrium states with finite superconducting coherence, are direct experimental manifestations of our theoretical predictions here, not captured by previously used

Anderson pseudospin models or perturbative Raman expansions. They arise at seventh-order or higher in any expansion and demonstrate that Cooper pair center-of-mass acceleration by the oscillating THz field, not captured by the Anderson pseudo-spin precession models or susceptibility expansions used so far, is important and must be treated non-perturbatively, as it changes the entire collective superconducting state and its excitations. Our recent experiments demonstrated a robust gapless accelerated superfluid state that is protected from phonon scattering unlike for single electron acceleration. Motivated by these prior results showing a distinct behavior unique to superconductors, in this manuscript, we use a gauge-invariant non-adiabatic density matrix theory to calculate for the first time phase-coherent nonlinear 2D THz spectra of BCS superconductors and demonstrate the importance of pump-probe interference in generating high order nonlinear responses beyond fifth-order discussed before, which dominate above critical driving. By also including light-wave propagation effects inside the superconducting system via Maxwell's wave equations, we obtain self-consistent gauge-invariant superconductor Bloch equation that describe the 2D THz experimentally observable smoking-gun signatures of the nonlinear dynamical interplay of light-wave acceleration of a Cooper-pair condensate, Anderson pseudo-spin nonlinear precession, and electromagnetic pulse propagation inside the superconducting system. This interplay leads to THz dynamical symmetry breaking and is responsible for the transition in the lineshape of 2D THz spectra above critical pump driving, which has not been discussed before and is not captured by previously used theories. Here we use this quantum kinetic modeling to directly simulate for the first time 2D terahertz nonlinear experiments in superconductors beyond susceptibility/response function perturbative expansions, i.e. we directly calculate the experimentally measured coherent nonlinear differential transmission in the time domain. This allows us to analyze and predict smoking-gun spectral features separated from the rest in 2D frequency space, with unique temperature and electric field dependencies distinguished from the other peaks that are simultaneous observed in 2D frequency space, by proposing multi-dimensional THz spectroscopy experiments of superconductors for super-resolution ultrafast imaging and quantum tomography of higher correlation.

(2) Difference of our findings from previous 2D nonlinear spectroscopy results: As referee 2 nicely summarizes, the results of our quantum kinetic simulations of 2D spectroscopy, which has only become experimentally possible in superconductors very recently, show several new correlated wave-mixing peaks in the 2D spectra with distinct temperature and field dependencies. These signals emerge and separate from previously identified pump-probe, four-wave-mixing, and high-harmonic generation peaks known from previous 2D spectroscopy experiments, both in the optical and THz frequency range, with increasing pump-field strength. Most importantly, **a new strong peak emerges in the right bottom corner of the 2D spectra**, **in a spectral region without any previously discussed conventional wave-mixing signal close by**. This isolated signal only appears *above critical driving in superconductors*, and only if phase-controlled pump-probe THz modulation of the off-diagonal long-range order is included at or beyond seventh-order nonlinear response. This new peak is the most direct experimental evidence of light-induced pseudo-spin correlation between two SC excitations (quasi-particle and quasi-particle/Higgs). Its physical origin is discussed at length in the revised Supplementary Information and in the revised manuscript. In particular, this new peak is absent in any previous studies and could also be used as a smoking gun experimental signature of light-induced superconductivity in high temperature superconductors, when appropriate coupled degrees of freedom are included. In addition, in the presence of light-induced inversion-symmetry breaking via nonlinear and electromagnetic propagation processes, our results differ significantly from all prior works. While our previously calculated nonlinear and pump-probe spectra show second-harmonic generation signals and dc supercurrent peaks, our results in Fig.4 are new: they demonstrate that strong inversion-symmetry breaking peaks emerge at $\omega_t = \omega_H$, in seventh-order responses or beyond, when the inversion-symmetry is broken in our simulations via terahertz light-wave electromagnetic propagation inside the superconducting system. These new light-induced inversion-symmetry breaking nonlinear peaks provide direct experimental evidence for the Higgs collective mode and can also be used as a sensor for light-induced superconductivity.

(3) Broader impacts: The theoretical approach presented in the manuscript is not restricted to BCS superconductors with a single order parameter. It can be extended to study the THz-driven non-equilibrium dynamics in multi-band superconductors or in superconducting systems with multiple coupled order parameters. In such systems, strong coupling of additional degrees of freedom is expected to produce light-induced condensate states that can be characterized and controlled by measuring the temperature dependence of correlated wave-mixing peaks in 2D THz spectra and by comparing their spectral position, temperature, and field dependencies to those of pump-probe peaks simultaneously observed in 2D frequency space and the equilibrium order parameter. This manuscript also paves the way for steering a quantum system, during cycles of carrier wave oscillations, towards eigenstates that can form a momentum Floquet lattice analogous to the Brillouin zone. More generally, it has been theoretically shown that the dynamics of a Floquet system under ultrafast driving (fast compared with any local energy scale) is approximately governed by a prethermal Hamiltonian. By non-adiabatically steering the system towards such states during single cycles of lightwave oscillation, via the interference of phase-locked intense pulses as proposed here, and by using 2D THz spectroscopy to directly observe such effects experimentally, we provide a step towards practical Floquet engineering in a wide range of quantum materials. By using our developed numerical simulation tool to analyze all relevant experiments, it is possible to characterize and control nonequilibrium driven quantum states in a broad range of interesting quantum systems.

Change #1: To clarify the above important points and avoid any misunderstanding of our work, we have substantially rewritten the abstract and introduction and have made several changes throughout the manuscript and the supplementary information, highlighted by track-changes.

The paper is full of abbreviations which makes it difficult to read. Several important quantities, for example SC order parameter and Higgs frequency, etc., are not defined until the theory section. In the present form, it is difficult to follow the work. It is not clear which two SC excitations are being probed.

Our response (#2):

We thank the referee for pointing this out and for his/her suggestions on how to improve the presentation of our manuscript. We have rewritten the abstract and the introduction accordingly. All important quantities, like the superconducting order parameter and Higgs frequency, are now defined in the introduction, before the results section, and schematically illustrated in Fig.1b. We have also clarified which two SC excitations contribute to the correlated wave-mixing signal in the abstract. To be precise, the correlated wave-mixing peak is driven by a source term proportional $\Delta\rho_2(k)\delta|\Delta_{pp}|^2$ in the equation of motion, as shown in full detail in the Supplementary Information. Here, $\Delta\rho_2(k)$ describes the pump-induced precession of the pseudo-spins away from their equilibrium x–z plane orientations (the pseudo-spin formalism is discussed in more detail in our response #). The coherent modulation of the superconducting order parameter, $\delta|\Delta_{pp}|$, is driven by the difference-frequency nonlinear process $2\omega_p - (\omega_p - \omega_{pro})$. Here the $2\omega_p$- process describes the excitation of a quasi-particle pair, whose energy is determined by the pump laser frequency independent of the pump-field strength. The quasi-particle excitation is facilitated by the phase-coherent sum-frequency Raman process of pump and probe pulses, $(\omega_p + \omega_{pro})$. The pump-induced pseudo-spin precession leads to a finite deviation $\Delta\rho_2(k)$ as in Anderson's original paper referenced in the manuscript, which introduced the pseudospin mechanism. This transverse pseudospin component oscillates at the Higgs frequency ω_H and describes both quasi-particle and/or Higgs collective excitations. In contrast to the $2\omega_p$- process discussed above, the energy of the ω_H – excitation process is strongly pump field dependent, as it depends on the quenched non-equilibrium superconductor order parameter. The correlated wave-mixing signals of main interest here result from seventh or higher order nonlinear responses generated by light-induced correlation between the SC excitation ω_H (quasi-particle pair or Higgs excitation), the quasi-particle pair excitation driven by the light field at $2\omega_p$, and the phase-coherent sum-frequency nonlinear Raman excitation process $\omega_p + \omega_{pro}$.

Change #2: To add clarity to the above important points, we have substantially rewritten the abstract and introduction and made changes throughout the manuscript, highlighted by track-changes. In particular, the superconducting order parameter and Higgs frequency are now defined in the introduction and schematically illustrated in Fig.1b. We also clarify which two superconductor excitations contribute to the correlated wave-mixing signals, in the abstract and introduction.

In the Methods, it is shown that the SC order-parameter can be expressed in terms of one of the four PS components. Can the authors comment on the physical interpretation of these components and clarify why only one specific component is related to the order-parameter and why electric current in Eq. (9) is related to the zeroth component? Are they related to the spin-spin correlations?

Our response (#3):

We thank the referee for the opportunity to clarify this important point, which makes our work more accessible to non-specialists. The non-equilibrium dynamics of superconductors is traditionally described by using the pseudo-spin formalism, which has been introduced by Anderson in our cited reference Phys. Rev. **112**, 1900–1916 (1958). This paper introduced the pseudo-spin description of superconductors and their excitations, which has been adopted by prior works in this field. Here, the pseudo-spin operators, derived by expanding the density matrix as in any qubit analysis, act in an imaginary space and are not related to a real physical spin operator. Instead, up and down pseudo-spins correspond to filled and empty electronic **k**-states, while tilted/canted spins correspond to a quantum superposition of up and down pseudo-spins. In the conventional pseudo-spin model, which does not take into account the condensate acceleration treated here leading to time-dependent translation of populations and coherences in momentum space, the BCS Hamiltonian is given by $H_{BCS} = \sum_k \sigma_k \cdot B_k$ where $\sigma = (\sigma_{k,1}, \sigma_{k,2}, \sigma_{k,3})$ is the Anderson pseudo-spin projected onto the Bloch sphere and $B_k = (-\Delta', -\Delta'', (\varepsilon_{k+p_S} + \varepsilon_{k-p_S})/2)$ is the pseudo-magnetic field acting onto σ_k. Here, Δ' and Δ'' are the real and imaginary parts of the coherent SC order parameter $\Delta = \Delta' + i\Delta'' = g\sum_k \sigma_{k,1} + i\sigma_{k,2}$, while ε_k is the band dispersion and p_S is the condensate momentum induced by the pump pulse. $\sigma_{k,3}$ corresponds to the occupation of state $\boldsymbol{k}$, while $\sigma_{k,1}$ and $\sigma_{k,2}$ describe the off-diagonal coherences which determine the superconducting order parameter.

In this standard approach to pseudo-spin nonlinearities within the conventional Anderson picture, the condensate momentum p_S defines a transverse light-induced magnetic field component that triggers the pseudo-spin precession. In the normal state, all $\boldsymbol{k}$-states with $|\boldsymbol{k}| < k_F$, where k_F is the Fermi wavevector, are occupied, while all the states $|\boldsymbol{k}| > k_F$ are empty. As a result, all pseudo-spins are up for $|\boldsymbol{k}| < k_F$ and down for $|\boldsymbol{k}| > k_F$ as illustrated in Fig.R1b. In contrast, each pseudo-spin is aligned along the pseudo-magnetic field in the BCS state, as shown in Fig.R1a and R1c. The non-equilibrium dynamics of the BCS superconductor within the Anderson pseudo-spin formalism is described by the Bloch equations, $\partial_t \sigma_k = 2B_k \times \sigma_k$. The nonlinear coupling between the applied light field and the pseudo-spin leads to pseudo-spin precession as illustrated in Fig.R1d.

Our model includes an important additional source of nonlinearity, which comes from THz light-wave acceleration of the macroscopic Cooper pair condensate. This nonlinear quantum transport effect introduces a condensate supercurrent flow driven by the light field. This photocurrent leads to periodically modulated nonlinearities corresponding to the time-dependent translation of the populations and coherences in momentum space arising from the acceleration of the collective condensate state. In particular, in the gauge-invariant Bloch equations presented in Eq.(S4), the acceleration of a macroscopic Cooper pair condensate leads to quantum transport driving terms of the form $E \cdot \nabla_k \rho_i$ absent in previously used conventional pseudospin theories and to coupling of different pseudo-pins, i.e., $\rho_i(k)$ at k and $k \pm p_S/2$, which are also absent in the conventional Anderson pseudospin models. Compared to these conventional pseudo-spin models, the light-induced Cooper-pair center-of-mass momentum dynamically breaks the equilibrium inversion symmetry, due to the preferred direction introduced by the strong linearly polarized THz electric field, such that the zeroth-order component of the pseudo-spin is not conserved anymore. As a result, our gauge-invariant equations of motion also include an equation of motion for the zeroth-order pseudo-spin component, which describes the dynamical coupling to the other pseudo-spin components that is present when quantum transport is considered. By expanding the density matrix in terms of pseudospin components similar to the standard analysis of a qubit, we make the connection with the previous works and also highlight the differences, which come from the quantum transport light-wave condensate acceleration component that is in addition to the conventional precession of Anderson pseudo-spins and leads to coupling pseudo-spins at different momentum points in the equations of motion. Furthermore, the addition of electromagnetic propagation effects breaks the equilibrium inversion symmetry even after the THz pulse and introduces a symmetry-breaking dc nonlinear photocurrent component.

The macroscopic electric current density is in the most general way defined as $J = e \sum_k \nabla_k \varepsilon(k + p_S/2) n_k$, where $\nabla_k \varepsilon$ is the group velocity and n_k is the *charge* density. By expressing this current in terms of the gauge-invariant density matrix, we obtain Eq.(S16). The time-evolution of this gauge-invariant nonlinear photocurrent driven by the THz field is fully determined by the dynamics of the zeroth-order component of the pseudo-spin. By expressing the current in terms of the original density matrix, Eq.(S17), we recover the results previously discussed within the traditional pseudo-spin models from our most general formulation, which also applies with quantum transport and light-induced inversion symmetry breaking included in addition to pseudo-spin precession.

Change #3: We have extended the discussion about the used Anderson pseudo-spin formalism in revised the manuscript and revised Supplementary Information to make our gauge-invariant density matrix approach more accessible to non-specialists.

It is mentioned that Eq. (6) is for homogenous system without justifying its use or giving any idea how it is obtained.

Our response (#4):

We thank the referee for the opportunity to clarify this point. The most general spatially-dependent gauge-invariant Bloch equations are discussed in detail in Ref. Phys. Rev. B 102, 054517 (2020). Here, the spatial dependence is treated by applying a gradient expansion. The relevant quantities, like order parameter, gauge-invariant density matrix, and electric field, are expanded in powers of $\nabla_R \cdot \nabla_k$ where R is the Cooper-pair center-of-mass coordinate. This expansion can be truncated whenever the characteristic length for the spatial variation of the SC condensate (center-of-mass) is larger than the coherence length of the Cooper pair (relative motion). In this manuscript, we assume a weak spatial dependence and thus neglect all spatially-dependent terms of order $\mathcal{O}(\nabla_R \cdot \nabla_k)$ and higher in the gradient expansion, which is a reasonable approximation for BCS *s*-wave superconductors. We also assume homogeneous excitation conditions, by neglecting any spatial *R*-dependence of the applied electric field. As a result of these reasonable approximations about the spatial dependence, we obtain the homogenous gauge-invariant Bloch equations Eq.(S4). The detailed derivation of the full spatially dependent gauge-invariant Bloch equations is presented in Phys. Rev. B 102, 054517 (2020) that describes our general theory in full detail.

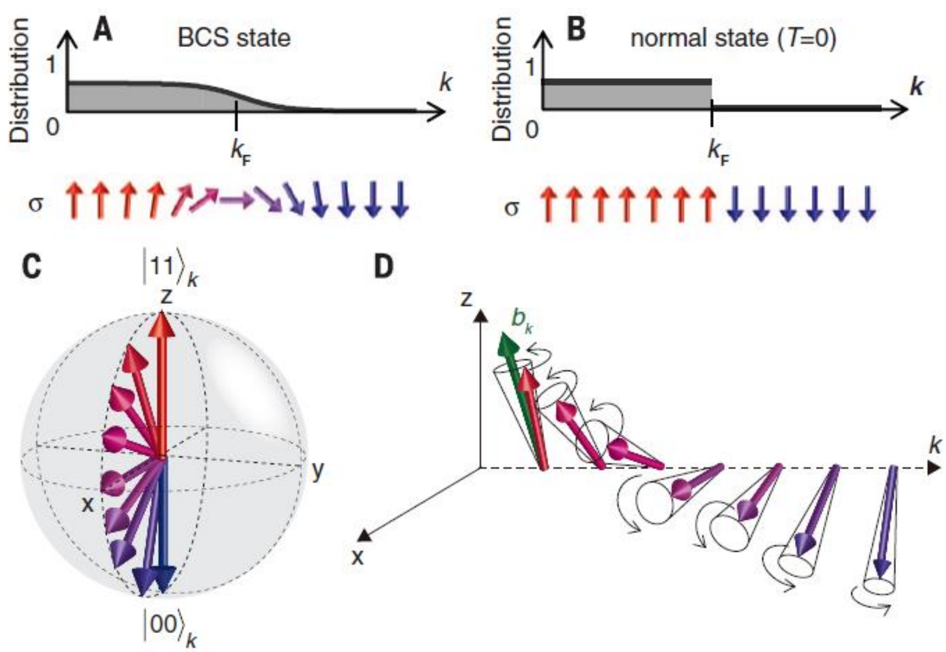

Figure R1 Pseudo-spin precession model used in standard literature (from Science **345**, 1145 (2014))

Change #4: We have added the above clarifications to the revised Supplementary Information.

The results reported in the manuscript may be correct but the presentation is too convoluted to follow. I do not recommend this work in its present form for publication.

Our response (#5):

We have significantly and thoroughly revised the manuscript and Supplementary Information to make the clarifications requested by the referee and to make references to prior literature that discusses the pseudo-spin model and our theory. We thank him/her for helping us improve our presentation and for clarifying some potential misunderstandings about our calculations. We believe that the revised manuscript is now easily accessible to the non-specialist.

Report of Reviewer #2

In the paper entitled "Visualization and Light-Driven Entanglement of Quantum Systems using Terahertz Multi-Dimensional Coherent Spectroscopy" by Martin Mootz, Liang Luo, Jigang Wang, and llias E. Perakis, the authors simulate Multi-Dimensional Coherent THz spectroscopy experiments. In particular, they use two phase-locked THz laser pulses to gain super-resolution visualization of nonequilibrium quantum states with dissipationless current flow coherently controlled via relative phase accumulation of two correlated excitations. They analyze the possibility of phase dependent tuning of photogenerated nonlinear interactions between SC excitations. In particular, they demonstrate the coherent steering of a superconducting state into tunable accelerated condensate states with THz inversion symmetry breaking during lightwave oscillation cycles. Above a critical driving, they find Correlated-Wave-Mixing and inversion-symmetry-breaking Wave Mixing peaks together with more conventional ones and consider these a possible way in the related experiment to detect the a THz-time-periodically-driven superconducting state. Moreover, they characterize these unconventional peaks and determine their source terms in the equations. These results are definitely novel and of interest to the community studying out-of-equilibrium superconductivity, but also to the wider community of researchers involved in (i) the characterization of the out-of-equilibrium response of and (ii) the optical control of unconventional materials. The references provided are adequate in number and span the proper portion of existing literature. The developed quantum kinetic modeling is very convincing and fully supports the drawn conclusions. Its comprehensiveness will definitely influence the field and set a new standard. I consider sufficient the level of detail provided in the main text and in the supplementary materials, together with the related references cited, to allow a researcher to reproduce the calculations. Accordingly, I do consider this paper acceptable for publication in Communications Physics in its current form.

Our response (#6): We thank the referee for his/her detailed assessment of our work and its novelty, and for nicely summarizing the crucial points made by our theoretical results that warrant publication in Communications Physics, as well as the wider impact of our results for the characterization of the out-of-equilibrium response and the optical control of unconventional quantum materials. We are pleased with his/her positive comments on the quality of our work and for recommending publication in Communications Physics.

Report of Reviewer #3

In their manuscript "Visualization and Light-Driven Entanglement of Quantum systems Using Terahertz Multi-Dimensional Coherent Spectroscopy," Martin Mootz and co-authors present a theoretical study of the types of things that it might be possible to see by applying Multi-Dimensional Coherent THz (MDC-THz) experiments to superconductors. The authors claim to be able to predict "experimental signatures of a THz-time-periodically-driven non-equilibrium [superconducting] state." The extension of multi-dimensional coherent spectroscopy techniques into the terahertz regime is a hot topic in ultrafast spectroscopy, with several different groups currently pursuing experiments of this sort. In order for these experiments to be able to be guided and interpreted, it is important to have a firm understanding of the spectroscopy technique's theoretical underpinnings, and so the topic presented by the authors is very welcome. Beyond this, recent studies into the possibility of using ultrafast pulses to induce superconductivity in different types of systems heightens the potential importance of this manuscript.

<u>Our response (#7):</u>

We are happy with the referee's appreciation of the significance of our results and grateful for his/her suggestions on how to improve the clarity of our manuscript.

Having noted these facts, however, the paper suffers from a severe lack of clarity to the point where I can barely understand at many points what the authors are trying to say. For example, the introductory paragraph is uncomfortably dense and jargon-heavy. There are excessive amounts of acronyms (SC, IS, CWM, ISWM, PP, FWM, HHG); there are far too many highly specialized terms for an introductory paragraph. Following the first paragraph, the language gets more plainspoken—which is welcome—but major sources of confusion remain. To pick on just one or two sentences: At the top of p. 3 the authors write that "one can steer the system into either [quasi-particle] or gapless- [superconducting] long-living such states…" I don't think it is possible to steer a system into a quasiparticle, nor do I understand from this phrasing what the authors are really trying to describe. Below this, the authors write that "…collective modes of [superconducting] states do not couple linearly to electromagnetic fields without finite Cooper-pair momentum. The latter can be induced…" It is not clear from this sentence whether "the latter" refers to "electromagnetic fields" or "finite Cooper pair momentum." Given the issues of confusion that I am left with after reading this manuscript, I unfortunately cannot recommend publication.

<u>Our response (#8):</u>

We thank the referee for pointing this out and for his/her suggestions on how to improve the presentation of our manuscript. We have significantly rewritten the entire manuscript to improve the readability of the story and highlight more clearly the key points of the study. We have revised all unclear sentences mentioned by the referee and have thoroughly rewritten the introductory paragraph, including reducing the use of the acronyms and specialized terms. We believe that the new introductory paragraph is now accessible to the general and non-expert audience. We would also like to stress that several points which distinguish our work from prior works make Communications Physics the right journal to publish this paper. Please see our response to Reviewer #1.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

I have gone through the resubmission by Perakis et al.
The manuscript reads much better now. The authors have responded well to all previous queries.
The work is interesting, timely and well written.
I recommend that this paper be accepted for publication

Reviewer #3 (Remarks to the Author):

This review corresponds to an assessment of the revised manuscript COMMSPHYS-21-0577A, submitted by Martin Mootz and co-authors to Communications Physics and now titled "Visualization and Light-Driven Entanglement of Quantum systems Using Terahertz Multi-Dimensional Coherent Spectroscopy."

The authors have done an admirable job of removing the barrage of acronyms that plagued the earlier rendition of their manuscript and so I can more effectively review the manuscript's content in this round of the review process. Remaining drawbacks to the manuscript are that the text remains dense, and in certain places the way that it conveys big ideas and overarching themes is still muddled, particularly in the first couple of paragraphs even after having been revised by the authors (see the detailed notes below). However, the topic of terahertz-frequency multi-dimensional coherent spectroscopy remains important field, and to date there has been little theoretical work addressing the kinds of signatures that one might expect to see using such techniques to study superconductors. The authors' underlying model is quite detailed in nature, appears to be scientifically sound, and suggests some interesting experimental signatures that might be worth seeking out. The revised manuscript therefore strikes me as being of sufficient value to the scientific community overall to be published in Communications Physics.

Detailed comments on text readability:

It may be useful in the introductory paragraph to more explicitly indicate that this is a purely theoretical work that is currently done.

In the second sentence, the authors write that "exotic correlations are masked by multiple contributions to nonlinear processes." The statement seems to imply that exotic correlations "are masked" from visibility using laser spectroscopy in all cases, which undercuts the following sentence. I suggest the authors add some qualifiers to this second sentence, better explaining when and how the exotic correlations are often masked.

A few sentences below this, in the sentence "These peaks split from conventional pump–probe peaks above critical tera- hertz driving, as determined by the electromagnetic field phase" I have a hard time telling whether the peak-shift is identified by looking at the electromagnetic field phase, or whether the electromagnetic field phase is used to determine critical terahertz driving threshold. I suggest the authors clarify their meaning.

The authors have made a lot of progress since the first iteration of the manuscript, but lots of other little changes like this might still have a significant positive impact on the readability of the manuscript. The level of readability improves significantly in the “Results” section and beyond.

Visualization and Quantum Control of Light-Accelerated Condensates by Terahertz Multi-dimensional Coherent Spectroscopy by Martin Mootz, Liang Luo, Jigang Wang, and Ilias E. Perakis

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Report of Reviewer #1

I have gone through the resubmission by Perakis et al. The manuscript reads much better now. The authors have responded well to all previous queries. The work is interesting, timely and well written. I recommend that this paper be accepted for publication

Our response (#1):

We thank the referee for offering careful reading of our manuscript and are pleased that he/she recommends publication in Communication Physics.

Report of Reviewer #3

This review corresponds to an assessment of the revised manuscript COMMSPHYS-21-0577A, submitted by Martin Mootz and co-authors to Communications Physics and now titled "Visualization and Light-Driven Entanglement of Quantum systems Using Terahertz Multi-Dimensional Coherent Spectroscopy."

The authors have done an admirable job of removing the barrage of acronyms that plagued the earlier rendition of their manuscript and so I can more effectively review the manuscript's content in this round of the review process. Remaining drawbacks to the manuscript are that the text remains dense, and in certain places the way that it conveys big ideas and overarching themes is still muddled, particularly in the first couple of paragraphs even after having been revised by the authors (see the detailed notes below). However, the topic of terahertz-frequency multi-dimensional coherent spectroscopy remains important field, and to date there has been little theoretical work addressing the kinds of signatures that one might expect to see using such techniques to study superconductors. The authors' underlying model is quite detailed in nature, appears to be scientifically sound, and suggests some interesting experimental signatures that might be worth seeking out. The revised manuscript therefore strikes me as being of sufficient value to the scientific community overall to be published in Communications Physics.

Our response (#2):

We appreciate the referee's critical reading and nice summary of the significance of our work. We are grateful for his/her suggestions on how to further improve the readability of our manuscript and are glad that he/she recommends publication in Communications Physics.

Detailed comments on text readability:

It may be useful in the introductory paragraph to more explicitly indicate that this is a purely theoretical work that is currently done.

In the second sentence, the authors write that “exotic correlations are masked by multiple contributions to nonlinear processes.” The statement seems to imply that exotic correlations “are masked” from visibility using laser spectroscopy in all cases, which undercuts the following sentence. I suggest the authors add some qualifiers to this second sentence, better explaining when and how the exotic correlations are often masked.

A few sentences below this, in the sentence “These peaks split from conventional pump–probe peaks above critical tera- hertz driving, as determined by the electromagnetic field phase” I have a hard time telling whether the peak-shift is identified by looking at the electromagnetic field phase, or whether the electromagnetic field phase is used to determine critical terahertz driving threshold. I suggest the authors clarify their meaning.

The authors have made a lot of progress since the first iteration of the manuscript, but lots of other little changes like this might still have a significant positive impact on the readability of the manuscript. The level of readability improves significantly in the “Results” section and beyond.

Our response (#3):

We thank the referee for his/her suggestions on how to further improve the presentation of our manuscript. We have rewritten the introductory paragraphs of the manuscript as suggested to improve the readability and to clarify all remaining confusion. We have also revised all unclear sentences mentioned by the referee.

It may be useful in the introductory paragraph to more explicitly indicate that this is a purely theoretical work that is currently done.

We have revised the third sentence of the introductory paragraph, starting with “Here…”, to make it clear that this paper is theoretical work: “Here we develop density matrix simulations to show that…”. We also added a clarification about this paper reporting theoretical work in the last sentence of the introductory paragraph: “Our theory suggests to use…”

In the second sentence, the authors write that “exotic correlations are masked by multiple contributions to nonlinear processes.” The statement seems to imply that exotic correlations “are masked” from visibility using laser spectroscopy in all cases, which undercuts the following sentence. I suggest the authors add some qualifiers to this second sentence, better explaining when and how the exotic correlations are often masked.

We have completely rewritten this sentence as suggested by the referee. The new sentence reads: “Although conventional static and ultrafast spectroscopy gives access to collective excitations characterizing quantum states, more exotic correlations cannot be easily separated from other contributions.”

A few sentences below this, in the sentence “These peaks split from conventional pump–probe peaks above critical tera- hertz driving, as determined by the electromagnetic field phase” I have a hard time telling whether the peak-shift is identified by looking at the electromagnetic field phase, or whether the electromagnetic field phase is used to determine critical terahertz driving threshold. I suggest the authors clarify their meaning.

We have completely rewritten the sentence as follows:

“Above critical terahertz driving, these emerging peaks split from conventional peaks along the second axis introduced by pump-probe relative phase in two-dimensional frequency space.”

Finally, we carefully went through the entire paper, especially the part before the Results section suggested by the referee, to ensure that every sentence is clear.