Non-perturbative terahertz high-harmonic generation in the three-dimensional Dirac semimetal Cd$_3$As$_2$

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Harmonic generation is a general characteristic of driven nonlinear systems, and serves as an efficient tool for investigating the fundamental principles that govern the ultrafast nonlinear dynamics. Here, we report on terahertz-field driven high-harmonic generation in the three-dimensional Dirac semimetal Cd$_3$As$_2$ at room temperature. Excited by linearly-polarized multi-cycle terahertz pulses, the third-, fifth-, and seventh-order harmonic generation is very efficient and detected via time-resolved spectroscopic techniques. The observed harmonic radiation is further studied as a function of pump-pulse fluence. Their fluence dependence is found to deviate evidently from the expected power-law dependence in the perturbative regime. The observed highly non-perturbative behavior is reproduced based on our analysis of the intraband kinetics of the terahertz-field driven nonequilibrium state using the Boltzmann transport theory. Our results indicate that the driven nonlinear kinetics of the Dirac electrons plays the central role for the observed highly nonlinear response.
n atomic gases, high-harmonic radiation is produced via a three-step process of ionization, acceleration, and recollision by a strong-field infrared laser. This mechanism has been intensively investigated in the extreme ultraviolet and soft X-ray regions, forming the basis of attosecond research. The observed high-harmonic generation was interpreted with fundamentally different mechanisms, such as interband tunneling combined with dynamical Bloch oscillations and intraband thermodynamics, and nonlinear dynamics, and many-body electronic interactions. Here, in a distinctly different context of a three-dimensional Dirac semimetal, we report on experimental observation of high-harmonic generation up to the seventh order driven by strong-field terahertz pulses. The observed non-perturbative high-harmonic generation is interpreted as a generic feature of terahertz-field-driven nonlinear intraband kinetics of Dirac fermions. We anticipate that our results will trigger great interest in detection, manipulation, and coherent control of Dirac and Weyl materials.

High-harmonic generation (HHG) in two-dimensional Dirac semimetals (single-layer graphene and 45-layer graphene) has been reported very recently for pump pulses both in the terahertz (10^{-12} Hz, 1 THz ~4 eV) and mid-infrared or near-infrared (0.2–0.8 eV) ranges. Although previous theoretical investigations pointed out that the peculiar linear energy-momentum dispersion relation (Dirac cone) should be essential for HHG in graphene (see e.g., ref. 25), the strong dependence on pump laser frequencies observed in the experiments favors different mechanisms. For the mid-infrared or near-infrared HHG, the interband transitions (combined with Bloch oscillations) play the crucial role, while the linear dispersion relation is not a prerequisite. A similar mechanism involving interband transitions can also be applied to a terahertz (THz) HHG in lightly-doped multi-layer graphene, whereas the electron distribution was found to play only a minor role. In contrast, for heavily electron-doped graphene, intraband processes become important and HHG ascribed to THz-field heated hot-electrons while assuming the electron subsystem thermalized quasi-instantaneously.

One may expect to observe THz HHG universally in the Dirac materials also of higher dimension, e.g., three-dimensional (3D) Dirac or Weyl semimetals. However, THz HHG so far has not been reported for this class of materials, and the mechanism for observing THz HHG in a 3D Dirac material remains elusive. Here, we report on time-resolved detection of non-perturbative THz HHG in the 3D Dirac semimetal Cd_{3}As_{2}, and a real-time theoretical analysis of the THz-field driven kinetics of the Dirac fermions that is directly linked to the linear dispersion relation. Our results show that the THz-field driven nonlinear kinetics of the Dirac electrons is the mechanism responsible for the efficient generation of high-harmonic radiation, as well as for its non-perturbative fluence dependence in Cd_{3}As_{2}.

### Results

**Third harmonic generation.** As being both theoretically predicted and experimentally confirmed, Cd_{3}As_{2} is a well-established room-temperature 3D Dirac semimetal with Fermi velocity about 10^{5} to 10^{6} m/s. Very compelling topological properties such as topological surface states and 3D quantum Hall effects have been realized in this system. In high-quality Cd_{3}As_{2} thin films prepared by molecular beam epitaxy, we observe HHG unprecedentedly up to the seventh order in the non-perturbative regime. THz harmonic radiation was recorded with femtosecond resolution at room temperature. Figure 1a displays the detected electric field as a function of time delay for the third harmonic radiation, induced by a multi-cycle pump pulse (Fig. 2a) with a peak field of 144 kV/cm characterized by its central frequency of f = 0.67 THz (Fig. 1b). The power spectrum of the harmonic radiation is obtained by Fourier transformation of the time-domain signals, which exhibits a sharp peak at 3f = 2.01 THz (Fig. 1b). The intensity of the harmonic radiation is nearly independent on the polarization of the pump pulse within the sample surface (see Supplementary Fig. 2). To further characterize the third harmonic generation, we measured the time-resolved signals for different pump-pulse intensities. As summarized in Fig. 1c, the fluence dependence of the third harmonic radiations remarkably does not follow the cubic law, but exhibits a power-law dependence as I_{3f} \propto I_{p}^{2.5} on the pump-pulse intensity I_{p}, which reveals a non-perturbative nonlinear response.

**THz driven nonlinear kinetics.** To understand the non-perturbative harmonic generation, we performed real-time theoretical analysis of the THz-driven kinetics of the 3D Dirac electrons. For the electron-doped system, interband electronic excitations are Pauli-blocked for one-photon transitions in the THz frequency range, thus we focus on the intraband kinetics of the nonequilibrium state by adopting a statistical approach of the Boltzmann transport theory. The initial state of thermodynamic equilibrium is defined by the room-temperature Fermi-Dirac distribution f_{0}(ε(p)) = \left[1 + \exp(\frac{ε-ε_{F}}{k_{B}T})\right]^{-1} for the 3D Dirac electrons obeying the linear dispersion relation ε(p) = v_{F}|p|, with p and v_{F} denoting momentum and Fermi velocity, respectively, ε_{F} for Fermi energy, k_{B} the Boltzmann constant, and T for temperature. In presence of the THz pulse, the driven transient state is characterized by the distribution function f(t, p), the time-dependent...
Higher-order harmonic generation. In order to detect higher-order harmonic radiation, we utilized lower-frequency and strong-field THz pump pulses (see "Methods"). Figure 3a shows the observed harmonic radiation up to the seventh order for the pump-pulse frequency of 0.3 THz (see Fig. 3b for the waveform).
Only the odd-order harmonics are observed, providing the spectroscopic evidence for the existence of inversion symmetry in the crystalline structure of Cd$_3$As$_2$ (see ref. 33). Our experimental results not only set the record for THz HHG in the 3D Dirac materials, but also present the striking observation of the non-perturbative fluence dependence for all the observed harmonic orders, as presented in Fig. 3c–e.

For the third harmonic radiation, the fluence dependence is also slightly below the cubic power-law dependence, similar to the behavior for the 0.7 THz pump pulse. Moreover, for the higher-order harmonics, the deviation from the corresponding perturbative power-law dependence is further increased. These features are perfectly captured by our quantitative theoretical analysis. By implementing the experimental pump pulse (see Fig. 3b) in our calculations, the time-resolved harmonic signals are derived as a function of pump-pulse fluence. The best fitting for all the experimentally observed HHG is achieved at $\tau = 10$ fs (see Fig. 3c–e). The obtained value of $\tau = 10$ fs is comparable to that in graphene as directly obtained via time-resolved and angle-resolved photoemission spectroscopic measurements43. While such measurements have not been reported in Cd$_3$As$_2$, an estimate based on the Shubnikov-de Haas measurements provides a $\tau$ value of the same order49. These results strongly indicate that the THz field-driven nonlinear kinetics of the Dirac electrons is the mechanism responsible for the observed non-perturbative nonlinear response in Cd$_3$As$_2$. Although for the seventh harmonic the experimental uncertainty is enhanced at the lowest fluence, the fluence dependence far away from the perturbative one is a clear and consistent experimental and theoretical observation. The non-perturbative response could be qualitatively understood in a way that the effective nonlinear susceptibilities are also function of the THz field due to the higher-order nonlinear response. We note that the observed non-perturbative response suggests that the experimental setting is close to but still below the so-called high-harmonic plateau regime, in which the HHG intensity remains almost constant for the high orders and drops abruptly at a cutoff frequency as found in gases as well as in solids1,20.

**Discussion**

The established mechanism of THz HHG here based on the driven nonlinear kinetics of Dirac electrons is different from those mechanisms proposed for HHG in graphene7,14,16,17, in which either the interband transitions were found playing the dominant role or the intraband electron subsystem is assumed to thermalize quasi-instantaneously. In contrast, in the context of the 3D Dirac system, we found that, firstly, in the presence of strong THz fields, the entire intraband distribution is strongly stretched and highly asymmetric, denying a description using the Fermi-Dirac distribution of thermodynamic equilibrium states that is symmetric along the Dirac cone. Secondly, for the intraband kinetics, the linear energy–momentum dispersion is crucial for the THz HHG, whereas for a parabolic dispersion in the single-particle picture, the induced radiation field $E_{\text{rad}} \propto \frac{d^2r}{dt^2} \propto \frac{d^2r}{dt^2} \propto F_{\text{in}}^2$ should follow the pump field $E_{\text{in}}$ hardly yielding harmonics. Thirdly, the exact shape of the electron distribution and its real-time evolution, as obtained from the Boltzmann transport theory, is directly responsible for the THz HHG. A higher efficiency is revealed for the cases of a more strongly stretched and highly asymmetric distribution, due to stronger THz electric field and/or reduced scattering rate.

In conclusion, we have observed THz driven HHG up to the seventh order unprecedentedly in the 3D Dirac semiconductor Cd$_3$As$_2$. The fluence dependence of all the observed HHG was found well beyond the perturbative regime. By performing real-time quantitative analysis of the THz field-driven intraband kinetics of the Dirac electrons using the Boltzmann transport theory, we have established the nonlinear intraband kinetics as the mechanism for the observed THz HHG in Cd$_3$As$_2$. The mechanism found here for THz HHG is expected to be universal in the vast family of 3D Dirac and Weyl materials44, which provides strategies for pursuing high efficiency of THz HHG, and establishes HHG as a sensitive tool for exploring the interplay of various degrees of freedom. Towards the high electric-field regime, an experimental realization of THz HHG plateau in the Dirac materials and a full quantum-mechanical dynamic analysis are still outstanding from both the fundamental and the application points of view. Recently, non-perturbative THz third-harmonic generation in Cd$_3$As$_2$ was also reported in Ref. 45.
Methods

Terahertz spectroscopy: We performed terahertz THz HHG experiments with THz sources based on a femtosecond laser system and on a linear electron accelerator. For the former, broadband THz radiation was generated through tilted pulse front scheme utilizing lithium niobate crystal. With initial laser pulse energy around 1.5 mJ at 800 nm central wavelength and 100 fs duration broadband THz radiation with up to 3 μJ pulse energy was generated. At the linear accelerator in Helmholtz Zentrum Dresden-Rossendorf, multi-cycle superintense THz pulses were generated in an undulator from ultra-short relativistic electron bunches. The generated THz radiation is carried envelope phase stable, linearly polarized with tunable emitted radiation frequency. The accelerator was operated at 100 kHz and was synchronized with an external femtosecond laser system. The latter served as probe in electro-optical sampling. To achieve high level of synchronization, a pulse-resolved detection scheme was employed. To produce narrow-band THz radiation, corresponding bandpass filters were used (see Supplementary Fig. 1 for more information).

Sample preparation and characterization: High-quality thin films of CdAS were grown by PerkinElmer (Waltham, MA) 425B molecular beam epitaxy system. The substrate of fresh-cleaned 2-inch mica (~70 μm in thickness) was annealed at 300 °C for 30 min to remove absorbed molecules. Then 10 nm-thick CdTe was deposited as buffer layer before the CdAS growth. CdAS bulk material (99.999%, American Elements Inc., Los Angeles, CA) was evaporated on to CdTe at 170 °C. The growth was in situ monitored by reflection high-energy electron diffraction (RHEED) system. The sample surface is parallel to the crystallographic (112) plane. Part of the sample was patterned in Hall bar geometry and performed in the THz electric field E. In order to solve this equation, we Fourier transform the distribution function \( f(t, p) \) = \( \frac{1}{Z} \int d\Omega \int d\mathbf{p} \mathcal{Z}(i\mathbf{p}) \exp(iz\mathbf{p}) \), which gives an ordinary differential equation

\[
\left( \frac{\partial}{\partial t} + \frac{1}{\tau} \right)f - iz e E \cdot \mathbf{v} = \frac{\dot{\mathbf{p}}}{\tau},
\]

where the electric field \( E \) has been set along the \( z \) direction.

The collision integral of the present equilibrium solution is solved numerically with the experimental THz fields as an input. Having the distribution function, we calculate its moments to get current density. The expression for current density has the following form

\[
\mathbf{j}(t) = -e \int \frac{d\mathbf{p}}{(2\pi)^3} \mathcal{Z}(i\mathbf{p}) \mathbf{p} f(t, \mathbf{p}),
\]

where \( \mathbf{p} \) denotes the unit vector along the momentum direction.

Kinetic theory: Our theoretical analysis employed a statistical approach of the semiclassical Boltzmann transport theory with an effective relaxation time. The semiclassical description of particles is captured by a single particle distribution function \( n_t(\mathbf{r}, \mathbf{p}) \) in phase space. Observables can be calculated as integrals over momentum space. In order to calculate \( f(t, \mathbf{r}, \mathbf{p}) \) one needs to solve the Boltzmann equation

\[
\frac{df}{dt} = \nabla E \cdot \mathbf{v} + \nabla f \cdot \mathbf{v} + \nabla f / \tau = -\frac{\partial}{\partial E} \mathcal{Z}(E, \mathbf{p}) + \frac{\partial}{\partial E} \mathcal{Z}(E, \mathbf{p}) - \mathcal{Z}(E, \mathbf{p}),
\]

with the electromagnetic fields \( E \) and \( \mathbf{B} \), the Berry curvature \( \Omega \), the Planck constant \( h \), and the elementary charge \( e \). \( \mathcal{Z}(E, \mathbf{p}) \) denotes the dispersion relation and \( D = 1 + \frac{\mathbf{B} \cdot \mathbf{v}}{\tau} \) is the modified phase space volume element. For the linearly polarized THz waves, we consider the dominant effects of the electric field while neglecting the magnetic field in our further analysis. Consequently, the (inverted) equations of motion take the following simple form

\[
\dot{\mathbf{r}} = \mathbf{v} \mathcal{Z}(E, \mathbf{p}) - e E \mathbf{v} = -e \mathbf{E}.
\]

Since we are interested in a homogenous solution, only the equation for \( \mathbf{p} \) is incorporated in the Boltzmann equation. The equation for \( \mathbf{r} \) is used to define the current density as follows:

\[
\mathbf{j}(t) = -e \int \frac{d\mathbf{p}}{(2\pi)^3} \mathcal{Z}(E, \mathbf{p}) \mathbf{p} f(t, \mathbf{p}).
\]

Nevertheless, it can be shown that the second theorem in this equation (proportional to \( E \times \mathbf{v} \mathcal{Z} \)) does not contribute to \( \mathbf{j}(t) \) in the case of linearly polarized THz pulse, corresponding to the present experimental setting. Therefore, for the particular experiment being reported now, we can write

\[
\mathbf{j}(t) = -e \int \frac{d\mathbf{p}}{(2\pi)^3} \mathcal{Z}(E, \mathbf{p}) \mathbf{p} f(t, \mathbf{p}) - e E \mathbf{v}.
\]

For the THz frequencies in our experiments, interband electronic transitions are Pauli-blocked for the electron-doped CdAS samples. Thus, to study the intraband electron dynamics, it is justified to adopt only linear scale.

References

1. Corkum, P. B. & Krausz, F. Attosecond science. Nat. Phys. 3, 381–387 (2007).
2. Drescher, M. et al. X-ray pulses approaching the attosecond frontier. Science 291, 1923–1927 (2001).
3. Paul, P. M. et al. Observation of a train of attosecond pulses from high harmonic generation. Science 292, 1689–1692 (2001).
4. Ghimire, S. et al. Observation of high-order harmonic generation in a bulk crystal. Nat. Phys. 7, 138–141 (2011).
5. Schubert, O. et al. Sub-cycle control of terahertz high-harmonic generation by dynamical Bloch oscillations. Nat. Photonics 8, 119–123 (2014).
6. Matsuura, R. et al. Light-induced collective pseudospin precession resonating with Higgs mode in a superconductor. Science 345, 1145–1149 (2014).
7. Bowland, P. et al. Ultrafast terahertz response of multilayer graphene in the nonperturbative regime. Phys. Rev. B 89, 041408 (2014).
8. Vampa, G. et al. Linking high harmonics from gases and solids. Nature 522, 462–464 (2015).
9. Langer, F. et al. Extreme ultraviolet high-harmonic spectroscopy of solids. Nature 521, 498–502 (2015).
10. Hohenleutner, M. et al. Real-time observation of interfering crystal electrons in high-harmonic generation. Nature 523, 572–575 (2014).
11. You, Y. S., Reis, D. A. & Ghimire, S. Anisotropic high-harmonic generation in bulk crystals. Nat. Phys. 13, 345–349 (2016).
12. Langer, F. et al. Lightwave-driven quasiparticle collisions on a subcycle timescale. Nature 533, 225–229 (2016).
13. Giorgianni, F. et al. Strong nonlinear terahertz response induced by Dirac surface states in Bi2Se3 topological insulator. Nat. Commun. 7, 11421 (2016).
14. Yoshikawa, N., Tamaya, T. & Tanaka, K. High-harmonic generation in graphene enhanced by elliptically polarized light excitation. Science 356, 726–738 (2017).

15. Rajasekaran, S. & et al. Probing optically silent superfluid stripes in cuprates. Science 359, 575–579 (2018).

16. Haefl, H. A. et al. Extremely efficient terahertz high-harmonic generation in graphene by hot Dirac fermions. Nature 561, 507–511 (2018).

17. Sovi, G. et al. Broadband, electrically tunable third-harmonic generation in graphene. Nat. Nanotechnol. 13, 583–588 (2018).

18. Chu, H. et al. Phase-resolved Higgs response in superconducting cuprates. Nat. Commun. 11, 1793 (2020).

19. Yang, X. et al. Lighthouse-driven gapless superconductivity and forbidden quantum beats by terahertz symmetry breaking. Nat. Photonics 13, 707–713 (2019).

20. Ghimire, S. & Reis, D. A. High-harmonic generation from solids. Nat. Phys. 15, 10–16 (2019).

21. Vampa, G. et al. Theoretical analysis of high-harmonic generation in solids. Phys. Rev. Lett. 113, 073901 (2014).

22. Huttner, U., Kira, M. & Koch, S. W. Ultrahigh off-resonant field effects in semiconductors. Laser Photon Rev. 11, 1700049 (2017).

23. Kemper, A. F. et al. Theoretical description of high-order harmonic generation in solids. N. J. Phys. 15, 023003 (2013).

24. Silva, R. E. F. et al. High-harmonic spectroscopy of ultrafast many-body dynamics in strongly correlated systems. Nat. Photonics 12, 266–270 (2018).

25. Mikhailov, S. & Ziegler. K. Nonlinear electromagnetic response of graphene: frequency multiplication and the self-consistent-field effects. J. Phys. 20, 384208 (2020).

26. Ishikawa, K. L. Nonlinear optical response of graphene in time domain. Phys. Rev. B 82, 201402 (2010).

27. Al-Naib, I., Poehmann, M. & Dignam, M. M. Optimizing third-harmonic generation at terahertz frequencies in graphene. Phys. Rev. B 91, 205407 (2015).

28. Wang, Z. et al. Three-dimensional Dirac semimetal and quantum transport in Cd3As2. Phys. Rev. B 88, 125427 (2013).

29. Ali, M. N. et al. The crystal and electronic structures of Cd3As2, the three-dimensional electronic analogue of graphene. Inorg. Chem. 53, 4062–4067 (2014).

30. Liu, Z. K. et al. A stable three-dimensional topological Dirac semimetal Cd3As2. Nat. Mater. 13, 677–681 (2014).

31. Borisenko, S. et al. Experimental realization of a three-dimensional Dirac semimetal. Phys. Rev. Lett. 113, 027603 (2014).

32. Neupane, M. et al. Observation of a three-dimensional topological Dirac semimetal phase in high-mobility Cd3As2. Nat. Commun. 5, 3786 (2014).

33. Crassee, L. et al. 3D Dirac semimetal Cd3As2: a review of material properties. Phys. Rev. Mater. 2, 120302 (2018).

34. Moll, P. J. W. et al. Transport evidence for Fermi-arc-mediated chiral transfer in the Dirac semimetal Cd3As2. Nature 535, 266–270 (2016).

35. Zhang, C. et al. Evolution of Weyl-orbit and quantum Hall effect in Dirac semimetal Cd3As2. Nat. Commun. 8, 1272 (2017).

36. Zhang, C. et al. Quantum Hall effect based on Weyl orbits in Cd3As2. Nature 565, 331–336 (2018).

37. Uchida, M. et al. Quantum Hall states observed in thin films of Dirac semimetal Cd3As2. Nat. Commun. 8, 2277 (2017).

38. Schumann, T. et al. Observation of the Quantum Hall effect in confined films of the three-dimensional Dirac semimetal Cd3As2. Phys. Rev. Lett. 120, 016801 (2018).

39. Liu, Y. et al. Gate-tunable quantum oscillations in ambipolar Cd3As2 thin films. NPG Asia Mater. 7, e221 (2015).

40. Bhatnagar, P. L., Gross, E. P. & Krook, M. A model for collision processes in gases. I. Small amplitude processes in charged and neutral one-component systems. Phys. Rev. 94, 511 (1954).

41. Xiao, D., Chang, M.-C. & Niu, Q. Berry phase effects on electronic properties. Rev. Mod. Phys. 82, 1959 (2010).

42. Green, B. et al. High-field high-repetition-rate sources for the coherent THz control of matter. Sci. Rep. 6, 22536 (2016).

43. Gierz, I. et al. Snapshots of non-equilibrium Dirac carrier distributions in graphene. Nature 12, 1119–1214 (2013).

44. Armitage, N. P., Mele, E. J. & Vishwanath, A. Weyl and Dirac semimetals in three-dimensional solids. Rev. Mod. Phys. 90, 015001 (2018).

45. Cheng, B. et al. Efficient Terahertz Harmonic Generation with Coherent Acceleration of Electrons in the Dirac Semimetal Cd3As2. Phys. Rev. Lett. 124, 117402 (2020).

46. Hinz, H. et al. Single-cycle terahertz pulses with amplitudes exceeding 1 MV/cm generated by optical rectification in LiNbO3. Appl. Phys. Lett. 98, 091106 (2011).

47. Yeh, K.-L. et al. Generation of 10 µJ ultrashort terahertz pulses by optical rectification. Appl. Phys. Lett. 90, 171121 (2007).

48. Kamprath, T., Tanaka, K. & Nelson, K. A. Resonant and nonresonant control over matter and light by intense terahertz transients. Nat. Photonics 7, 680–690 (2013).

49. Kovalchv, S. et al. Probing ultra-fast processes with high dynamic range at 4th-generation light sources: arrival time and intensity binning at unprecedented repetition rates. Struct. Dyn. 4, 024301 (2017).

50. Duval, C. et al. Berry phase correction to electron density in solids and “exotic” dynamics. Mod. Phys. Lett. B20, 373 (2006).

51. Stefhanov, M. A. & Yin, Y. Chiral kinetic theory. Phys. Rev. Lett. 109, 162001 (2012).

52. Logayanagam, R. & Surwówka, P. Anomaly/transport in an Ideal Weyl gas. JHEP 04, 097 (2012).

53. Dantas, R. M. A. et al. Magnetotransport in multi-Weyl semimetalic: a kinetic theory approach. JHEP 12, 069 (2018).