

Ultrafast photoexcitation of semiconducting photocathode materials

Hilde Bellersen ^{1,2,*}, Michele Guerrini^{1,†} and Caterina Cocchi ^{1,2,‡}

¹*Carl von Ossietzky Universität Oldenburg, Institute of Physics, 26129 Oldenburg, Germany*

²*Friedrich-Schiller Universität Jena, Institute for Condensed Matter Theory and Optics, 07743 Jena, Germany*



(Received 12 March 2025; revised 28 May 2025; accepted 1 July 2025; published 22 July 2025)

Cs-based semiconductors like Cs₃Sb and Cs₂Te are currently used as photocathodes in particle accelerators. Their performance as electron sources critically depends on their interaction with intense laser sources. However, detailed studies on their strong-field excitation dynamics are currently missing. In this work, we employ real-time time-dependent density functional theory to investigate from first principles the time-dependent response of Cs₃Sb and Cs₂Te to ultrafast pulses of varying intensities, ranging from 1 GW/cm² to 1 PW/cm². Our analysis reveals that nonlinear effects, including high-harmonic generation, emerge with intensities of 100 GW/cm² in Cs₃Sb and 200 GW/cm² in Cs₂Te. We show that beyond these thresholds, the excitation mechanisms evolve from one-photon absorption saturation to increasingly dominant multiphoton absorption (above 1 TW/cm² for Cs₃Sb and 5 TW/cm² for Cs₂Te). Under the highest field intensities (>10 TW/cm²), the onset of tunnel ionization is identified through occupation analysis. These findings offer material-specific insights into the nonlinear optical properties and nonequilibrium electron distributions in the femtosecond regime of these photocathode materials, providing valuable indications to optimize their performance and stability as high-brightness electron sources.

DOI: [10.1103/449c-nn6y](https://doi.org/10.1103/449c-nn6y)

I. INTRODUCTION

Ultrabright electron beams generated by radio-frequency (rf) photoinjectors are an important tool in modern material science, offering a powerful way to explore in great detail the fundamental properties of different classes of compounds [1,2]. They are an essential part of advanced synchrotron facilities and free-electron lasers around the world [3–5], where most of such experiments are performed. In rf photoinjectors, electrons are released from the photocathode through the photoelectric effect. The emitted electrons are then accelerated by strong electric fields, giving rise to ultrabright electron beams. High-quality beams are achieved with high peak current for reduced gain length, low emittance for a small beam cross section, and a narrow energy spread [4,6,7]. Since the beam quality is directly linked to the properties of the photocathode, it is essential to select and optimize its composition and characteristics appropriately. This need has driven extensive research in the last decade, focused on developing materials with high quantum efficiency, long durability, low thermal emittance, and fast response times [4,8–12].

While metals are the most established photocathode materials [4,13], current trends in accelerator physics increasingly

favor alkali-based semiconductors, thanks to their high quantum efficiency and ability to produce low-emittance beams at high repetition rates [4,11,14]. Cs₂Te and Cs₃Sb are among the most studied compounds because they offer high quantum efficiency, good thermal stability, durability, and reliable performance [15–18]. The rise of these materials has received essential support from computational studies based on *ab initio* methods such as density-functional theory (DFT) and many-body perturbation theory, which have contributed to shed light on their fundamental properties, including their electronic structure, vibrational properties, and response to radiation [19–32].

For a complete understanding of light-matter interactions in Cs₂Te and Cs₃Sb, it is important to analyze their nonlinear response to ultrafast coherent pulses of varying intensities approaching or even overcoming those impinging on the photocathodes to produce electron beams. The most suitable *ab initio* scheme for this purpose is real-time time-dependent DFT (RT-TDDFT) [33], which provides a reliable description of the evolution of the electron density subject to an external time-dependent electric field of tunable frequency, polarization, shape, duration, and intensity. Being a nonperturbative approach, RT-TDDFT delivers the complete response of the material including nonlinear effects [34]. While initially implemented for confined systems like molecules and clusters [35], this formalism has been successfully applied to several classes of crystalline materials, ranging from bulk semiconductors [36–38] and insulators [39,40] to monolayers [41–43] and their heterostructures [44–46].

In this work, we study from first principles the excited-state dynamics of Cs₂Te and Cs₃Sb crystals impinged by femtosecond pulses in resonance with their dominant absorption peaks in the ultraviolet (UV) and visible region. Our

*Contact author: hilde.bellersen@uni-jena.de

†Contact author: michele.guerrini@uni-oldenburg.de

‡Contact author: caterina.cocchi@uni-jena.de

goal is to address the following pressing questions that are crucial for the development of high-performance photocathodes: (i) What are the strong-field excitation dynamics in these materials? (ii) How do different excitation mechanisms contribute to their electronic response under high-intensity UV/visible lasers? (iii) What are the nonequilibrium electron distributions ruling the ultrafast dynamics in Cs-based semiconducting photocathodes? To address these points, we adopt the nonperturbative framework of RT-TDDFT. By irradiating the systems with pulsed radiation ranging in intensity from 1 GW/cm² up to 1 PW/cm², we thoroughly investigate the nonlinear optical response of these materials, focusing on relevant phenomena like high-harmonic generation and multi-photon absorption. Exploring such a broad power range, even beyond the operational intensities of photocathodes in particle accelerators, is essential for systematically mapping the transition from weak to strong light-matter coupling regimes and for determining the intensity threshold above which the electronic response becomes distinctly nonlinear. Through the analysis of critical quantities such as the number of excited electrons and absorbed photons, we estimate the absorption efficiency as a function of the laser intensity, identifying and discussing key mechanisms ultimately affecting the operational performance of semiconducting photocathodes for ultrabright electron beams.

II. COMPUTATIONAL METHODS

A. Theoretical background

The calculations presented in this study are based on DFT [47,48] and RT-TDDFT [49] as implemented in the OCTOPUS code [50] adopting a real-space grid representation for the electron density. Linear absorption spectra are computed by perturbing the systems with an instantaneous broadband electric field (δ kick) in the velocity gauge [33]. The optical conductivity $\sigma(\omega)$ is obtained by dividing the current density by the incident electric field $\mathcal{E}(\omega)$ induced by the δ kick:

$$\sigma(\omega) = \frac{J(\omega)}{\mathcal{E}(\omega)}. \quad (1)$$

The imaginary part of the dielectric function $\varepsilon(\omega)$ is related to the real part of the optical conductivity by the conventional formula:

$$\text{Im}[\varepsilon(\omega)] = \frac{4\pi\Omega}{\mathcal{E}_0\omega} \text{Re}[\sigma(\omega)], \quad (2)$$

where ω is the frequency of the incoming radiation, Ω the unit-cell volume, and $\mathcal{E}_0$ the amplitude of $\mathcal{E}(\omega)$.

The time-dependent response of the system under an ultrafast electric field is evaluated by applying a vector potential [51] satisfying the usual relation

$$\mathcal{E}(t) = -\frac{d\mathbf{A}(t)}{dt}. \quad (3)$$

The microscopic current density

$$\mathbf{j}(\mathbf{r}, t) = \frac{1}{2N_k} \sum_{n\mathbf{k}} \left[\phi_{n\mathbf{k}}^*(\mathbf{r}, t) \left(-i\nabla + \frac{\mathbf{A}(t)}{c} \right) \phi_{n\mathbf{k}}(\mathbf{r}, t) + \text{c.c.} \right] \quad (4)$$

is obtained from the solutions of the time-dependent Kohn-Sham (KS) equations [52], $\phi_{n\mathbf{k}}(\mathbf{r}, t)$, where N_k is the total number of k points sampling the Brillouin zone. Integrating Eq. (4) over the unit-cell volume Ω leads to the time-dependent macroscopic current density

$$\mathbf{J}(t) = \frac{1}{\Omega} \int_{\Omega} \mathbf{j}(\mathbf{r}, t) d^3r, \quad (5)$$

which enters the expression of the high-harmonic generation (HHG) spectrum,

$$H(\omega) = \left| \int_0^\infty \frac{\mathbf{J}(t)}{dt} e^{-i\omega t} dt \right|^2, \quad (6)$$

obtained from the squared Fourier transform of the macroscopic current density in Eq. (5).

The population of the time-dependent KS states is obtained from their projection onto the ground-state KS states at $t = 0$:

$$\mathcal{P}_{n,\mathbf{k}}(t) = \sum_{n'}^{\text{occ}} |\langle \phi_{n\mathbf{k}}(t=0) | \phi_{n'\mathbf{k}}(t) \rangle|^2. \quad (7)$$

The occupation density is given by the ground-state density of states weighted by $\mathcal{P}_{n,\mathbf{k}}(t)$:

$$\mathcal{N}(\epsilon, t) = \sum_{n,\mathbf{k}}^{\text{all}} \delta(\epsilon - \epsilon_{n,\mathbf{k}}^0) \mathcal{P}_{n,\mathbf{k}}(t), \quad (8)$$

while the number of excited electrons per unit cell is obtained by summing $\mathcal{P}_{n,\mathbf{k}}(t)$ over all unoccupied states:

$$N_{\text{ex}}(t) = \sum_{n,\mathbf{k}}^{\text{unocc}} \mathcal{P}_{n,\mathbf{k}}(t). \quad (9)$$

The time-dependent energy per unit volume absorbed by the system from the field corresponds to the difference between the total energy at a certain time t after the perturbation and the ground-state energy, $\Delta E(t) = E(t) - E_{\text{GS}}$. This quantity is related to the total current and the external field via

$$\Delta E(t) = \int_0^t \mathbf{J}(t') \cdot \mathcal{E}(t') dt'. \quad (10)$$

The number of photons absorbed by the irradiated material is the ratio between ΔE , evaluated at the end of the pulse propagation ($t = t_{\text{fin}}$), and the energy associated with the carrier frequency of the applied field ($\hbar\omega_0$):

$$N_{\text{ph}} = \frac{\Delta E(t_{\text{fin}})}{\hbar\omega_0}. \quad (11)$$

The number of incoming photons is estimated by calculating the total energy of the pulse, E_{pulse} , obtained by integrating the intensity over time and multiplying it by the effective unit-cell area A , divided by the photon energy $E_{\text{photon}} = \hbar\omega_0$,

$$N_{\text{ph}}^{\text{in}} = \frac{E_{\text{pulse}}}{E_{\text{photon}}} = \frac{I\sqrt{2\pi}\tau_0 A}{\hbar\omega_0}, \quad (12)$$

where I is the peak intensity of the pulse and τ_0 is the standard deviation of the Gaussian envelope. The photon absorption efficiency is finally defined as the ratio between the number

of absorbed and incident photons:

$$\mathcal{A}_{ph} = \frac{N_{ph}}{N_{ph}^{in}}. \quad (13)$$

It is worth noting that, in this theoretical approach, electron-hole correlations are not explicitly accounted for. In dedicated work [25], it was clarified that excitonic effects have only a minor impact on the linear absorption of both Cs_3Sb and Cs_2Te , mainly consisting of an expected redshift of the spectral weight, with relative energies and intensities of the interband transitions remaining unaffected. By pumping the systems resonantly with excitations well above the spectral onset and probing their response nonperturbatively, we can exclude the possibility that excitonic effects substantially alter the results presented in this study. Conversely, in the calculation of susceptibility tensors, which is not undertaken here, electron-hole interactions could play an important role [53].

B. Computational details

Ground-state calculations are carried out on a real-space grid with 0.2 Å spacing and k -meshes with $5 \times 5 \times 5$ points for Cs_3Sb and $4 \times 6 \times 4$ points for Cs_2Te obtained from a modified version of the Monkhorst-Pack scheme [54]. Norm-conserving ONCV pseudopotentials [55] are used to treat core electrons, and the Perdew-Burke-Ernzerhof (PBE) approximation [56] is adopted for the exchange-correlation potential in DFT and for the exchange-correlation functional in RT-TDDFT. We did not include spin-orbit coupling based on previous findings [25,26] indicating a negligible role of this effect on the band structures of selected alkali-antimonides and -tellurides. On this basis, we do not anticipate any relevant impact of this effect on the strong-field resonant dynamics investigated in this work. The lattice parameters of both materials are taken from Ref. [26] without performing any further optimization.

Linear absorption spectra are computed from RT-TDDFT, adopting the Yabana-Bertsch scheme [49] extended to solids [33]. The time propagation is carried out for 10 fs on both materials, adopting a time step of 1 as for Cs_3Sb and of 0.5 as for Cs_2Te . To minimize the numerical divergence at low frequencies, which is inherent to this method [57], in these runs, we increase the k -point density to $10 \times 10 \times 10$ points for Cs_3Sb and $5 \times 8 \times 4$ points for Cs_2Te . To probe their non-linear response, the systems are subsequently perturbed with an x -polarized pulse of Gaussian shape. The pulse applied on Cs_3Sb has its peak intensity at $t_0 = 18$ fs and a standard deviation $\tau_0 = 5$ fs, corresponding to a spectral width of about 360 meV. For Cs_2Te , the peak intensity of the pulse is set at $t_0 = 15$ fs and its standard deviation is $\tau_0 = 4$ fs, leading to a 450 meV bandwidth. The pulse frequency is set to 2.4 eV/ $\hbar$ for Cs_3Sb and 3.6 eV/ $\hbar$ for Cs_2Te , in resonance with the absorption maxima dominating the linear spectra of the two materials to ensure that the incoming energy is efficiently taken up. Pulses of increasing intensities are adopted, ranging from 1 GW/cm² to 1 PW/cm² and including several intermediate steps to determine the threshold of nonlinear response of both systems accurately. Time propagations are run for 70 fs for Cs_3Sb and 60 fs for Cs_2Te , with time steps ranging from 0.7 as to 2.2 as, depending on the laser intensity.

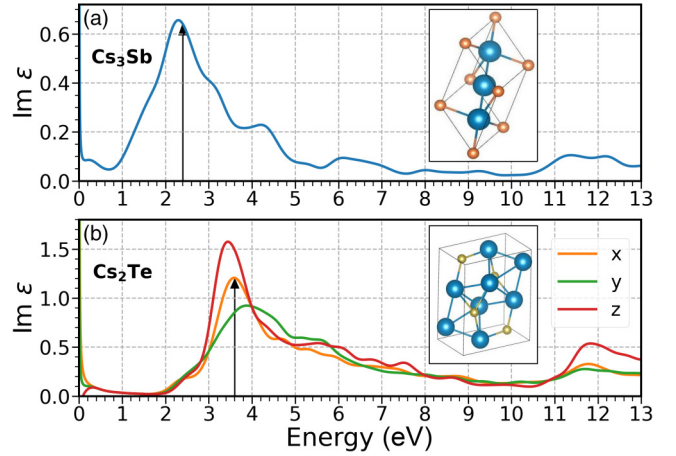


FIG. 1. Linear absorption spectra of (a) Cs_3Sb and (b) Cs_2Te calculated as the imaginary part of their macroscopic dielectric function. In contrast with cubic Cs_3Sb , characterized by a single inequivalent component of ϵ , the spectrum of orthorhombic Cs_2Te exhibits distinct contributions along each Cartesian direction. (insets) Ball-and-stick representations, generated with the visualization software VESTA [64], of the unit cells of (a) Cs_3Sb and (b) Cs_2Te , with Cs atoms depicted in blue, Sb atoms in orange, and Te atoms in gold.

III. RESULTS AND DISCUSSION

A. Structural properties

The crystal structure of Cs_3Sb consists of a face-centered cubic (fcc) lattice with space group $Fm\bar{3}m$, already adopted in previous theoretical studies [19,22,23,26,58] as a simplification of the cubic lattice originally proposed by Jack *et al.* [59]. The primitive unit cell, shown in the inset of Fig. 1(a), includes three Cs atoms at fractional positions $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ with the first and last being chemically equivalent [23], and one Sb atom located at the origin. The adopted lattice parameter of 9.298 Å is taken from the PBE results of Ref. [26]. This value overestimates the experimental reference by 1.18%, a known shortcoming of the PBE functional [60].

Cs_2Te belongs to the $Pnma$ space group and is characterized by an orthorhombic unit cell with lattice vectors $a = 9.542$ Å, $b = 5.845$ Å, and $c = 11.591$ Å taken from the PBE results of Ref. [26]. The unit cell, depicted in the inset of Fig. 1(b), includes eight Cs atoms and four Te atoms, and corresponds to the experimentally established Cs_2Te polymorph [61]. Other phases of this material, which have been computationally predicted to be stable [62], are not considered in this work. The band structures and density of states computed for both materials are visualized in Fig. S1 of the Supplemental Material [63].

B. Linear absorption spectra

The linear absorption spectrum of Cs_3Sb is dominated by a strong peak at 2.4 eV preceded by a shoulder around 1.5 eV [Fig. 1(a)]. Weaker maxima are found around 3 and 4.5 eV while deeper in the UV region, the material is almost transparent to radiation. The main absorption features displayed in Fig. 1(a) are consistent with those obtained from the GW approximation and the solution of the Bethe-Salpeter equation

[25], likely due to a mutual compensation of quasiparticle corrections and exciton binding energies.

The absorption spectrum of Cs_2Te [Fig. 1(b)] starts at approximately 2 eV and exhibits sharp maxima at 3.6 eV in the x polarization and at 3.45 eV along z . In the y direction, a broader peak appears at 3.9 eV. Similar to Cs_3Sb , also Cs_2Te is almost transparent to near-UV light except around 12 eV, where a weak maximum appears, especially in the z component. Due to larger and nonmatching values of quasiparticle corrections and exciton binding energies in this material, the agreement between Fig. 1(b) and results obtained in the framework of many-body perturbation theory [25] is worse than for Cs_3Sb . On the other hand, expectedly, the results plotted in Fig. 1(b) match very well the independent-particle spectra presented in Ref. [25]. When comparing absorption spectra computed from RT-TDDFT with those obtained from perturbative approaches, it is crucial to consider that, in the former, the spectral smearing is inherently determined by the finite duration of the time propagation while, in the latter, usually yielding δ -like excitations as eigenvalues of an effective Schrödinger equation [65], an artificial broadening is applied in postprocessing to obtain the desired spectral resolution.

Another important remark in this analysis concerns the finite values of the imaginary part of the dielectric function in the region near 0 eV, a known artifact of the adopted RT-TDDFT formalism. This spurious contribution is due to the finite duration of the time propagation used in the simulations [57], which introduces an artificial broadening that extends into the subgap energy region. To maintain full transparency regarding the results of the RT-TDDFT calculations and their inherent characteristics, we display in Fig. 1 the raw output of our runs without any filtering of unphysical points.

C. High-harmonic generation

With the knowledge of the linear optical properties of Cs_3Sb and Cs_2Te , we proceed with the analysis of their time-dependent response to an ultrafast electric field set in resonance with their most intense excitation in the UV-visible region (black arrows in Fig. 1). In the case of Cs_2Te , we excite the system along the x direction, targeting the maximum at 3.6 eV. We first examine the HHG spectra computed from Eq. (6), comparing the results obtained with four increasing laser intensities ranging from 1 GW/cm² to 100 TW/cm², see Fig. 2.

With the weakest pulse ($I = 1$ GW/cm²), the HHG spectrum of Cs_3Sb contains only the fundamental harmonic at $\hbar\omega_0 = 2.4$ eV, corresponding to the carrier frequency of the pulse [Fig. 2(a)]. In this linear regime, the response of the system can be described by the microscopic form of Ohm's law, where the current density is proportional to the applied electric field

$$J(\omega) = \sigma(\omega)\mathcal{E}(\omega), \quad (14)$$

consistent with Eq. (1). As shown in Fig. 2(b), by increasing the laser intensity to 100 GW/cm², higher harmonics are excited. Due to the inversion symmetry of the Cs_3Sb crystal, the second harmonic is silent while the third one is clearly visible at $3\hbar\omega_0 = 7.2$ eV. Further increase of the field intensity to 100 TW/cm² excites also the fifth harmonic, generating a

weak but distinct signal at $5\hbar\omega_0 = 12$ eV. These findings indicate a nonlinear response of the system, where the current density is no longer proportional to the applied electric field as in Eq. (14). Instead, the generation of higher harmonics indicates the appearance of nonlinear optical processes, involving both interband and intraband transitions [66,67].

By further increasing the laser intensity to 1 TW/cm², the magnitudes of the third and fifth harmonics increase, and higher harmonics up to the eleventh order are generated, see Fig. S2 of the Supplemental Material [63]. In the energy range visualized in Fig. 2(c), the seventh harmonic is visible at $7\hbar\omega_0 = 16.8$ eV in addition to the third and fifth ones. When the external field reaches the intensity of 100 TW/cm², the baseline of the HHG spectrum is significantly elevated across the entire frequency range shown in Fig. 2(d). In this case, the harmonic peaks become much less distinct due to strong-field effects, including enhanced ionization and tunneling [67]. The nonvanishing spectral components at frequencies corresponding to even high harmonics hint at a (dynamical) symmetry breaking in the density distribution of Cs_3Sb induced by the strong electric field [68], along with other complex nonlinear effects that cannot be straightforwardly singled out in the adopted nonperturbative approach.

The results obtained for Cs_2Te , displayed on the right side of Fig. 2, are qualitatively similar to those discussed above for Cs_3Sb . The weakest pulse intensity of 1 GW/cm² excites only the fundamental harmonic at $\hbar\omega_0 = 3.6$ eV [Fig. 2(e)]. With even harmonics being forbidden in the centrosymmetric Cs_2Te crystal, the third-harmonic signal at $3\hbar\omega_0 = 10.8$ eV is triggered by a laser intensity of 500 GW/cm² [Fig. 2(f)], which is a factor of 5 larger compared with the one needed to excite the same component in Cs_3Sb [Fig. 2(b)]. An intensity of 5 TW/cm² activates higher harmonics up to $7\hbar\omega_0 = 25.2$ eV, see Fig. 2(g). The HHG signal generated by $I = 100$ TW/cm² shows again an elevated baseline as in Cs_3Sb [compare Fig. 2(h) with Fig. 2(d)]. However, in contrast with Cs_3Sb , in the HHG spectrum of Cs_2Te , the peaks associated with the odd harmonics remain distinct from the background noise and minima appear at the energies of the even harmonics, suggesting a higher threshold for tunneling and ionization for this material.

Overall, the results presented in Fig. 2 indicate a higher HHG yield in Cs_2Te than in Cs_3Sb . This enhancement can be attributed to two main factors. First, the slightly higher atomic number of Te ($Z = 52$) compared with Sb ($Z = 51$) leads to a stronger electron-nuclear potential due to increased Coulomb interaction [69]. Although subtle, this effect cannot be ignored. Second, the lower proportion of Cs atoms with respect to the nonmetallic species in the unit cell of Cs_2Te compared with Cs_3Sb reduces the influence of delocalized Cs electrons, resulting in a greater contribution from the heavier Te atoms to the electron-nuclear potential, leading to a more pronounced spatial variation of the electron density.

D. Number of absorbed photons, number of excited electrons, and photon absorption efficiency

To further assess the nonlinear response of Cs_3Sb and Cs_2Te to resonant pulses of increasing intensity, we

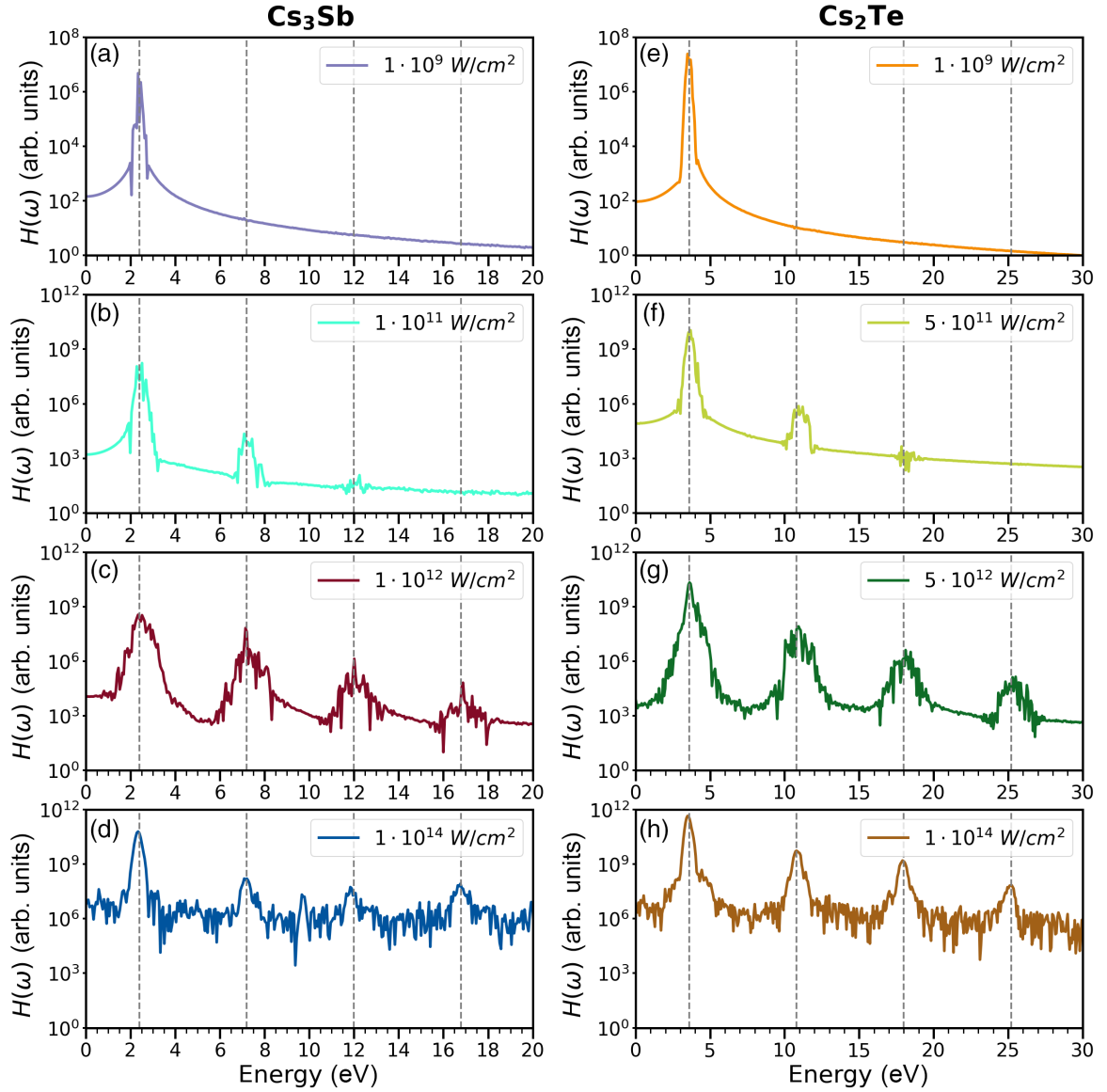


FIG. 2. HHG spectra of Cs_3Sb (left) and Cs_2Te (right) impinged by pulses with intensity (a) $I = 1 \text{ GW/cm}^2$, (b) $I = 100 \text{ GW/cm}^2$, (c) $I = 1 \text{ TW/cm}^2$, (d) $I = 100 \text{ TW/cm}^2$, (e) $I = 1 \text{ GW/cm}^2$, (f) $I = 500 \text{ GW/cm}^2$, (g) $I = 5 \text{ TW/cm}^2$, (h) $I = 100 \text{ TW/cm}^2$. The vertical dashed bars mark the energies of the fundamental harmonics and their odd multiples.

calculate macroscopic quantities such as the number of absorbed photons, the number of excited electrons, and the photon absorption efficiency per unit volume of each material, all evaluated after the pulse is turned off. The temporal evolution of $N_{ph}(t)$ and $N_{ex}(t)$ is shown in Figs. S3 and S4 of the Supplemental Material [63].

By inspecting Fig. 3(a), where the number of absorbed photons are displayed as a function of the laser intensity, we notice that in both Cs_3Sb and Cs_2Te , N_{ph} increases linearly up to $I = 100 \text{ GW/cm}^2$ in Cs_3Sb and up to $I = 200 \text{ GW/cm}^2$ in Cs_2Te . Beyond these values, N_{ph} reaches a plateau, suggesting the saturation onset for one-photon absorption, while multiphoton absorption remains negligible. At $I > 1 \text{ TW/cm}^2$ for Cs_3Sb and $I > 5 \text{ TW/cm}^2$ for Cs_2Te , weak multiphoton absorption starts to appear, as confirmed by the superlinear increase of the number of absorbed photons, $N_{ph}(I) \propto I^{1.2}$. The trends obtained for the two materials are quite similar

although in Cs_2Te , N_{ph} remains systematically higher than in Cs_3Sb .

The number of excited electrons displayed in Fig. 3(b) exhibits a more complex behavior. A linear increase proportional to the pulse intensity appears up to 100 GW/cm^2 for Cs_3Sb and 200 GW/cm^2 Cs_2Te , where $N_{ph}(I) \propto I$. Above these thresholds, N_{ex} forms a plateau similarly to N_{ph} , suggesting a saturation of the lowest unoccupied states due to Pauli blocking [37,46]. For $I > 1 \text{ TW/cm}^2$ and $I > 5 \text{ TW/cm}^2$, when multiphoton absorption comes into play, the number of excited electrons starts to increase linearly again due to excited-state absorption. Given the limited number of available electrons to be excited in this regime, N_{ex} grows less steeply than at weaker intensities, where absorption from the ground state dominates. Eventually, N_{ex} begins to saturate again at higher intensities, due to the finite number of electrons available in the unit cell. In Fig. 3(b), the number of

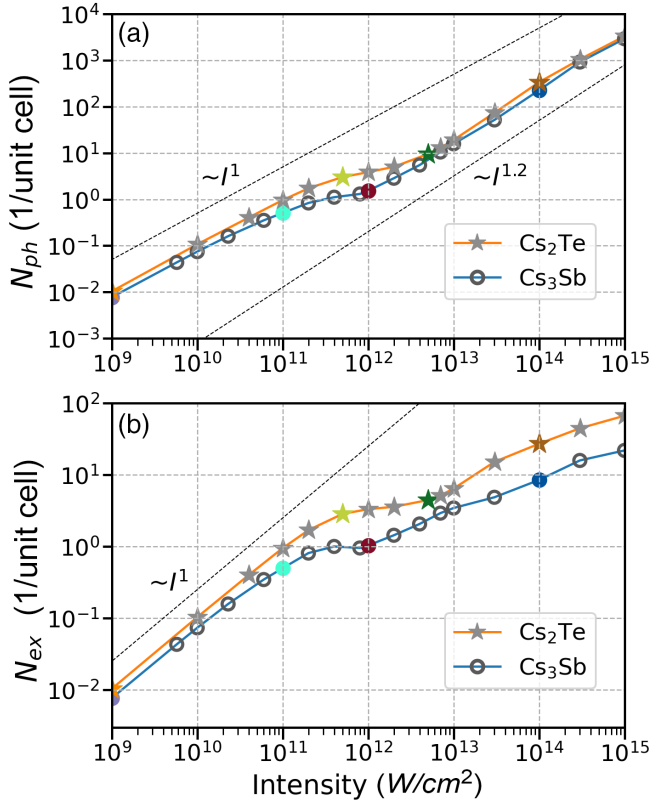


FIG. 3. (a) Number of absorbed photons N_{ph} and (b) number of excited electrons N_{ex} as a function of the laser intensity. Both quantities are evaluated at $t = 36$ fs, when the temporal extent of the pulse has concluded. Color-filled symbols are used for the intensities adopted to plot the HHG spectra (same color code used) while gray stars and hollow circles correspond to additional calculations performed to evaluate the overall trend. The solid colored lines are guides for the eyes, while the dashed lines indicate linear trends proportional to the indicated power of the laser intensity I .

excited electrons remains systematically larger for Cs_2Te than for Cs_3Sb , although the discrepancy between the two materials increases at higher intensities. This behavior is consistent with the fact that N_{ex} is directly related to the occupation density, see Eq. (9).

We finally inspect the intensity-dependent photon absorption efficiency given by the ratio between absorbed and incoming photons [Eq. (13)]. To perform this estimate, we take the effective area A , entering Eq. (13), as the cross-sectional area of the unit cell of each crystal normal to the x -polarized incoming laser. The resulting values are $22 \text{ \AA}^2$ for Cs_3Sb and $67.7 \text{ \AA}^2$ for Cs_2Te . As shown in Fig. 4, $\mathcal{A}_{ph}$ exhibits a similar behavior for both materials, starting with approximately constant (or, for Cs_2Te , even slightly increasing) values under weak intensities ($I \leq 10 \text{ GW/cm}^2$), followed by a monotonic but nonlinear decrease up to $I = 1 \text{ TW/cm}^2$ associated with the region of saturated absorption. The absorption efficiency of Cs_3Sb is initially higher than that of Cs_2Te impinged by weak laser intensities, but starts to decrease earlier, leading to a crossover at 50 GW/cm^2 . At $I = 2 \text{ TW/cm}^2$, the absorption efficiency of Cs_3Sb again surpasses the one of Cs_2Te and remains above it for all higher

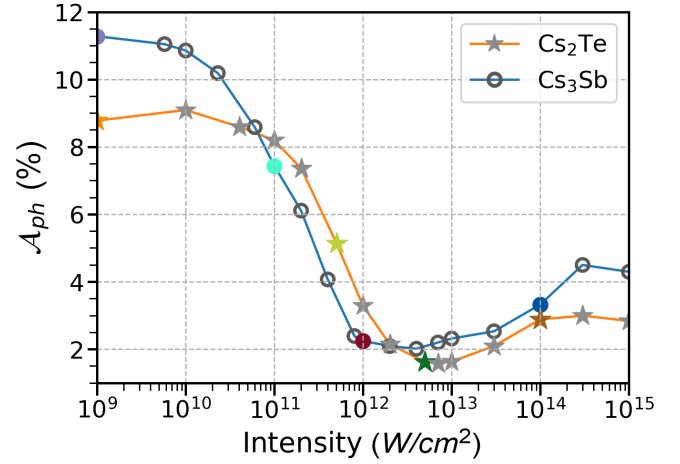


FIG. 4. Photon absorption efficiency $\mathcal{A}_{ph}$ as a function of the laser intensity in Cs_2Te (orange) and Cs_3Sb (blue). Color-filled symbols are used for the intensities adopted to plot the HHG spectra (same color code used) while gray stars and hollow circles correspond to additional calculations performed to evaluate the overall trend.

intensities. Local minima appear at approximately 4 TW/cm^2 in Cs_3Sb and 7 TW/cm^2 in Cs_2Te . In Cs_3Sb , the photon absorption efficiency is almost flat between $I = 1 \text{ TW/cm}^2$ and $I = 10 \text{ TW/cm}^2$. Above this value, it increases again in both materials, before forming another plateau between $I = 100 \text{ TW/cm}^2$ and $I = 1 \text{ PW/cm}^2$.

We can correlate this behavior with the trends collected for the HHG spectra, N_{ex} , and N_{ph} . In the weak-intensity range, where the response of the materials is linear ($I \leq 10 \text{ GW/cm}^2$), the photon absorption efficiency is maximized. Its steepest decrease appears for intensities triggering nonlinearities ($10 \text{ GW/cm}^2 < I \leq 1 \text{ TW/cm}^2$) but where one-photon absorption still dominates. At the threshold of the strong-coupling regime, where multiphoton processes become relevant ($I \approx 10 \text{ TW/cm}^2$), $\mathcal{A}_{ph}$ is minimized, due to the reorganization of the electronic structure. Multiphoton processes enable a further increase of the photon absorption efficiency between $I = 10 \text{ TW/cm}^2$ and $I = 100 \text{ TW/cm}^2$, where, however, the electronic structure of the material is irreversibly perturbed by the incoming radiation, as seen in the HHG spectra [Figs. 2(d) and 2(h)]. This effect is more pronounced in Cs_3Sb than in Cs_2Te .

The excitation dynamics discussed above are significantly influenced by the choice of a Gaussian pulse with a finite energy width impinging on both systems. Due to this characteristic, the perturbation excites multiple electronic states or even an entire excitation band, rather than just a single resonance. At high power, when nonlinear optical processes dominate, the coupled dynamics of the multiple excited states involved determines the response of the system. Moreover, considering the relatively high pulse frequency compared with the linear absorption onset of both Cs_3Sb and Cs_2Te , and the large excitation density of both materials in the energy range of the laser, decoupling the dynamics of a single resonance would have been a nontrivial task even by applying an extremely narrow-band pulse.

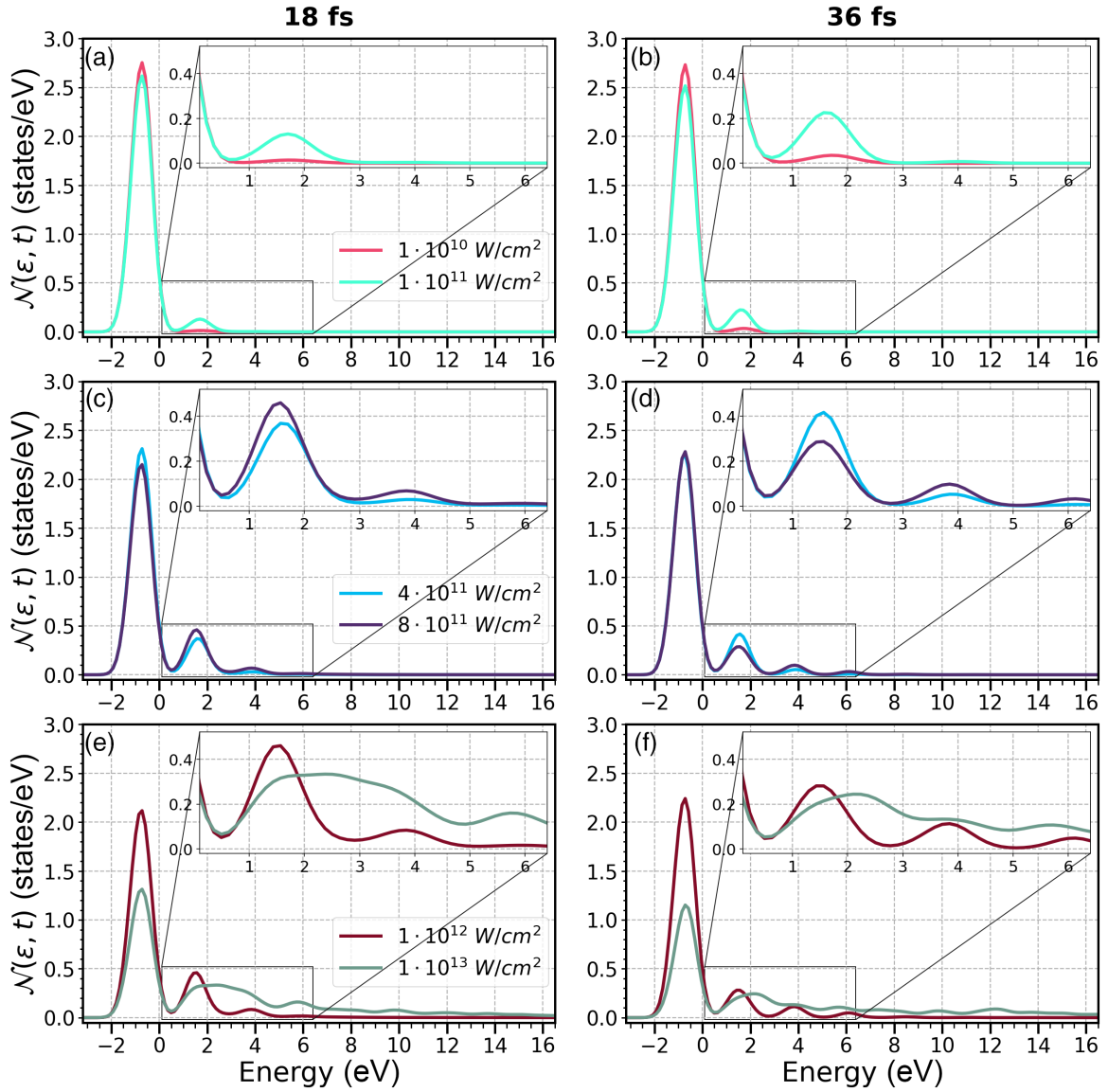


FIG. 5. Occupation density $\mathcal{N}(\epsilon, t)$ of Cs₃Sb computed at the peak of the incident pulse ($t = 18$ fs, left) and at the end of its propagation ($t = 36$ fs, right) with intensities (a), (b) $I = 10$ GW/cm² and $I = 100$ GW/cm²; (c), (d) $I = 400$ GW/cm² and $I = 800$ GW/cm²; and (e), (f) $I = 1$ TW/cm² and $I = 10$ TW/cm². A Gaussian broadening of 38 meV is applied to all curves to enhance visualization.

E. Occupation density

We finally inspect the occupation density at two relevant times, namely, when the pulse is at its peak value (18 fs) and when it is turned off (36 fs). Given the similarities between the two materials, we focus only on Cs₃Sb. The goal of this analysis is to gain insight into how the laser-excited electronic states redistribute over the unoccupied bands at increasing intensity of the incoming radiation, representing the regimes of weak, intermediate, and strong light-matter couplings.

When excited by the weakest pulses considered in this work, the optical response of Cs₃Sb is dominated by inter-band transitions, leading to a very small increase (≈ 0.01 with $I = 10$ GW/cm² and ≈ 0.1 with $I = 100$ GW/cm²) in the population of unoccupied states at approximately 1.5 eV above the valence-band maximum set to 0 eV. This behavior is consistent with the linear one-photon absorption at

$\hbar\omega_0 = 2.4$ eV. The conduction states are populated already when the pulse reaches its peak intensity [$t = 18$ fs, Fig. 5(a)] and remain partially occupied also after the laser is turned off [$t = 36$ fs, Fig. 5(b)]. However, the postpulse population of the conduction region increases roughly twice as much as that at 18 fs, indicating that most excited electrons remain there due to the absence of decay channels in our RT-TDDFT simulations. Due to charge conservation, the population of the conduction states is combined with a corresponding depletion of the valence-band maximum around -1 eV, see Figs. 5(a) and 5(b). We emphasize that the regions below and above 0 eV do not necessarily have equal areas as they represent densities and not charges. Instead, the absolute difference between the areas of the TDOS and occupation density below 0 eV should be equal to the area of the occupation density above 0 eV, meaning that the depletion of filled states compensates for the occupation of initially unoccupied states.

At the intermediate intensities of 400 and 800 GW/cm², when both N_{ph} and N_{ex} undergo saturation (Fig. 3), unoccupied states available at 3.9 eV are populated when the pulse reaches its peak [$t = 18$ fs, Fig. 5(c)], as a consequence of excited-state absorption. The overall occupation density in the conduction band becomes broader at $I = 800$ GW/cm², mirrored by a stronger depletion of the valence region. After the pulse is turned off at $t = 36$ fs, the valence-band population does not change further under either intensity. Still, there is a slight redistribution of the occupation in the conduction region, see Fig. 5(d). In particular, the population maximum 1.5 eV, associated with one-photon absorption, appears stronger for $I = 400$ GW/cm² than for $I = 800$ GW/cm², whereas at higher energies, the occupation density is larger when $I = 800$ GW/cm². This is consistent with the higher number of excited electrons but lower energy uptake at $I = 400$ GW/cm² (Fig. 3). At $I = 800$ GW/cm², additional population appears at 6.2 eV: this feature is ascribed to three-photon absorption. This result confirms the appearance of multiphoton absorption processes with intensities of 800 GW/cm² or higher.

The occupation density at 1 TW/cm² closely resembles the one at 800 GW/cm² with peaks at 1.5 eV (one-photon absorption), 3.9 eV (two-photon absorption), and 6.2 eV (three-photon absorption) appearing in decreasing intensity, see Fig. 5(c). Interestingly, also in this case, the population of states at 6.2 eV appears only after laser illumination [$t = 36$ fs, Fig. 5(f)], suggesting that the excitation mechanisms at these intensities are equally dominated by multiphoton absorption. A considerable change in the laser-driven occupation of the conduction region occurs at $I = 10$ TW/cm². At this intensity, the excited electron population is almost uniformly distributed up to 17.5 eV. This effect is more remarkable during irradiation [Fig. 5(e)] than after the pulse is turned off [Fig. 5(f)]. The peaks at 1.5, 3.9, and 6.2 eV merge into an almost featureless continuous distribution that can be associated with emerging tunnel ionization. In this strong-field regime, tunneling through the distorted Coulomb potential barrier of the nuclei occurs [39,70,71]. It is worth recalling that tunnel ionization depends on the field strength, not on the photon energy [72], leading to a broad and continuous energy distribution of the excited electrons. This effect is also consistent with the loss of space inversion symmetry of the density distribution already discussed in the context of the HHG spectra [Fig. 2(d)]. In this strong-field regime, tunnel ionization dominates and drives intraband electronic motion, which takes up a relevant role in the response of the system, and is responsible, among other effects, for the irregular behavior seen in the HHG spectra displayed in Fig. 2(d). Finally, a slight increase in the occupation density around 12.5 eV can be related to higher-order nonlinear processes and other complex light-matter interactions occurring in this strong-coupling regime. The valence-band population decreases accordingly, halving its value compared with the result obtained under weak laser intensity [compare Figs. 5(a) and 5(b)].

IV. SUMMARY AND CONCLUSIONS

In summary, we investigated from first principles the time-dependent response of Cs₃Sb and Cs₂Te to ultrafast laser

pulses of increasing intensities, ranging from 1 GW/cm² to 1 PW/cm², in order to explore different regimes of light-matter couplings. The energy and polarization of the incoming field were set in resonance with the strongest linear absorption maxima of the two materials at 2.4 eV for cubic Cs₃Sb and 3.6 eV for orthorhombic Cs₂Te, exciting this system with an x -polarized pulse. In this analysis, we monitored HHG, the number of absorbed photons, and the number of excited electrons per unit cell, as well as the photon absorption efficiency.

Up to $I = 100$ GW/cm², the response of the materials remains linear, as testified by the absence of high-harmonic peaks in the HHG spectra and by linear increases of both N_{ph} and N_{ex} upon increasing laser intensities. For $100 \text{ GW/cm}^2 \leq I \leq 1 \text{ TW/cm}^2$ in Cs₃Sb and $200 \text{ GW/cm}^2 \leq I \leq 5 \text{ TW/cm}^2$ in Cs₂Te, higher-harmonic peaks emerge in the HHG spectra and the scaling of absorbed photons and excited electrons becomes nonlinear, indicating one-photon absorption saturation and the onset of nonlinear effects. For intensities above these ranges, the response of the materials becomes markedly nonlinear. The HHG spectra exhibit strong peaks at high harmonics and prominent signatures of symmetry breaking in the electronic distribution. The number of absorbed photons increases superlinearly with respect to the intensity, while the number of excited electrons grows more slowly due to Pauli blocking. Finally, the electron occupation density in the conduction region of Cs₃Sb becomes significantly broader and extends almost homogeneously up to high energies (> 10 eV), suggesting the presence of multiphoton absorption and tunnel ionization effects.

In conclusion, this study provides crucial insights into the nonlinear optical properties of Cs₃Sb and Cs₂Te, particularly the initial electronic excitation and subsequent coherent dynamics under strong-field conditions induced by femtosecond pulses. Our results highlight the complex interplay between intense laser radiation and electronic structure, improving our insight into the ultrafast response of Cs-based photocathode materials under intense laser fields. This knowledge is essential to properly understand the longer timescale phenomena, including critical factors like damage thresholds, carrier recombination, which are crucial for the operational performance and stability of photocathodes.

ACKNOWLEDGMENTS

Useful discussions with Holger-Dietrich Saßnick in the initial stage of this project are kindly acknowledged. This work was funded by the German Research Foundation (DFG), Project No. 490940284, by the State of Lower Saxony (Professorinnen für Niedersachsen, DyNano, and EILiKo), and by the German Federal Ministry of Education and Research (Professorinnenprogramm III). Computational resources were provided by the HPC cluster ROSA at the University of Oldenburg, funded by the DFG (Project No. INST 184/225-1 FUGG) and the Ministry of Science and Culture of the State of Lower Saxony.

DATA AVAILABILITY

The data that support the findings of this article are openly available in Zenodo [73].

- [1] T. Tschentscher, C. Bressler, J. Grünert, A. Madsen, A. P. Mancuso, M. Meyer, A. Scherz, H. Sinn, and U. Zastrau, Photon beam transport and scientific instruments at the European XFEL, *Appl. Sci.* **7**, 592 (2017).
- [2] G. Sciaini, Recent advances in ultrafast structural techniques, *Appl. Sci.* **9**, 1427 (2019).
- [3] P. Emma, R. Akre, J. Arthur, R. Bionta, C. Bostedt, J. Bozek, A. Brachmann, P. Bucksbaum, R. Coffee, F.-J. Decker, Y. Ding, D. Dowell, S. Edstrom, A. Fisher, J. Frisch, S. Gilevich, J. Hastings, G. Hays, P. Hering, Z. Huang *et al.*, First lasing and operation of an Ångström-wavelength free-electron laser, *Nat. Photon.* **4**, 641 (2010).
- [4] D. Dowell, I. Bazarov, B. Dunham, K. Harkay, C. Hernandez-Garcia, R. Legg, H. Padmore, T. Rao, J. Smedley, and W. Wan, Cathode R&D for future light sources, *Nucl. Instrum. Methods Phys. Res., Sect. A* **622**, 685 (2010).
- [5] H. Zhang, S. Gilevich, A. Miahnahri, S. C. Alverson, A. Brachmann, J. Duris, P. Franz, A. Fry, J. Hirschman, K. Larsen, R. Lemons, S. Li, B. Lu, A. Marinelli, M. Martinez, J. May, E. Milshtein, K. Murari, N. Neveu, J. Robinson *et al.*, The LCLS-II photoinjector laser infrastructure, *High Power Laser Sci. Eng.* **12**, e51 (2024).
- [6] V. Ayvazyan, N. Baboi, I. Bohnet, R. Brinkmann, M. Castellano, P. Castro, L. Catani, S. Choroba, A. Cianchi, M. Dohlus, H. T. Edwards, B. Faatz, A. A. Fateev, J. Feldhaus, K. Flöttmann, A. Gamp, T. Garvey, H. Genz, C. Gerth, V. Gretchenko *et al.*, Generation of GW radiation pulses from a VUV free-electron laser operating in the femtosecond regime, *Phys. Rev. Lett.* **88**, 104802 (2002).
- [7] R. Alley, V. Bharadwaj, J. Clendenin, P. Emma, A. Fisher, J. Frisch, T. Kotseroglou, R. Miller, D. Palmer, J. Schmerge, J. Sheppard, M. Woodley, A. Yeremian, J. Rosenzweig, D. Meyerhofer, and L. Serafini, The design for the LCLS rf photoinjector, *Nucl. Instrum. Methods Phys. Res., Sect. A* **429**, 324 (1999).
- [8] R. Barday, A. Burrill, A. Jankowiak, T. Kamps, J. Knobloch, O. Kugeler, A. Matveenko, A. Neumann, M. Schmeißer, J. Völker, P. Kneisel, R. Nietubyc, S. Schubert, J. Smedley, J. Sekutowicz, and I. Will, Characterization of a superconducting Pb photocathode in a superconducting rf photoinjector cavity, *Phys. Rev. Spec. Top.–Accel. Beams* **16**, 123402 (2013).
- [9] M. A. H. Schmeißer, S. Mistry, H. Kirschner, S. Schubert, A. Jankowiak, T. Kamps, and J. Kühn, Towards the operation of Cs-K-Sb photocathodes in superconducting rf photoinjectors, *Phys. Rev. Accel. Beams* **21**, 113401 (2018).
- [10] E. R. Antoniuk, Y. Yue, Y. Zhou, P. Schindler, W. A. Schroeder, B. Dunham, P. Pianetta, T. Vecchione, and E. J. Reed, Generalizable density functional theory based photoemission model for the accelerated development of photocathodes and other photoemissive devices, *Phys. Rev. B* **101**, 235447 (2020).
- [11] G. Loisch, Y. Chen, C. Koschitzki, H. Qian, M. Gross, A. Hannah, A. Hoffmann, D. Kalantaryan, M. Krasilnikov, S. Lederer, X. Li, O. Lishilin, D. Melkumyan, L. Monaco, R. Niemczyk, A. Oppelt, D. Sertore, F. Stephan, R. Valizadeh, G. Vashchenko *et al.*, Direct measurement of photocathode time response in a high-brightness photoinjector, *Appl. Phys. Lett.* **120**, 104102 (2022).
- [12] J. Schaber, R. Xiang, and N. Gaponik, Review of photocathodes for electron beam sources in particle accelerators, *J. Mater. Chem. C* **11**, 3162 (2023).
- [13] J. R. Maldonado, Z. Liu, D. H. Dowell, R. E. Kirby, Y. Sun, P. Pianetta, and F. Pease, Robust CsBr/Cu photocathodes for the linac coherent light source, *Phys. Rev. Spec. Top.–Accel. Beams* **11**, 060702 (2008).
- [14] P. Musumeci, J. Giner Navarro, J. Rosenzweig, L. Cultrera, I. Bazarov, J. Maxson, S. Karkare, and H. Padmore, Advances in bright electron sources, *Nucl. Instrum. Methods Phys. Res., Sect. A* **907**, 209 (2018).
- [15] D. Filippetto, H. Qian, and F. Sannibale, Cesium telluride cathodes for the next generation of high-average current high-brightness photoinjectors, *Appl. Phys. Lett.* **107**, 042104 (2015).
- [16] E. Wisniewski, S. Antipov, M. Conde, D. Doran, W. Gai, C. Jing, W. Liu, J. Power, and C. Whiteford, Cs₂Te photocathode performance in the AWA high-charge high-gradient drive gun, *Proceedings of the 6th International Particle Accelerator Conference IPAC2015, USA* (JACoW, Richmond, VA, 2015), pp. 3283–3285.
- [17] Y. Liu, H. Tian, F. Li, G. Wang, and X. Wang, Effects of nanomaterials on Cs₃Sb photocathode emission performance, *AIP Adv.* **12**, 035004 (2022).
- [18] C. T. Parzyck, A. Galdi, J. K. Nangoi, W. J. I. DeBenedetti, J. Balajka, B. D. Faeth, H. Paik, C. Hu, T. A. Arias, M. A. Hines, D. G. Schlom, K. M. Shen, and J. M. Maxson, Single-crystal alkali antimonide photocathodes: High efficiency in the ultrathin limit, *Phys. Rev. Lett.* **128**, 114801 (2022).
- [19] L. Kalarasse, B. Bennecer, and F. Kalarasse, Optical properties of the alkali antimonide semiconductors Cs₃Sb, Cs₂K₂Sb, CsK₂Sb and K₃Sb, *J. Phys. Chem. Solids* **71**, 314 (2010).
- [20] S.-D. Guo, Electronic structures and elastic properties of X₃Sb (X = Li, K, Cs) from the first-principles calculations, *Mater. Res. Express* **1**, 015906 (2014).
- [21] C. Cocchi, S. Mistry, M. Schmeißer, J. Kühn, and T. Kamps, First-principles many-body study of the electronic and optical properties of CsK₂Sb, a semiconducting material for ultra-bright electron sources, *J. Phys.: Condens. Matter* **31**, 014002 (2019).
- [22] C. Cocchi, S. Mistry, M. Schmeißer, R. Amador, J. Kühn, and T. Kamps, Electronic structure and core electron fingerprints of caesium-based multi-alkali antimonides for ultra-bright electron sources, *Sci. Rep.* **9**, 18276 (2019).
- [23] C. Cocchi, X-ray absorption fingerprints from cs atoms in Cs₃Sb, *Phys. Status Solidi RRL* **14**, 2000194 (2020).
- [24] R. Amador, H.-D. Saßnick, and C. Cocchi, Electronic structure and optical properties of Na₂K₂Sb and NaK₂Sb from first-principles many-body theory, *J. Phys.: Condens. Matter* **33**, 365502 (2021).
- [25] C. Cocchi and H.-D. Saßnick, Ab initio quantum-mechanical predictions of semiconducting photocathode materials, *Micromachines* **12**, 1002 (2021).
- [26] H.-D. Saßnick and C. Cocchi, Electronic structure of cesium-based photocathode materials from density functional theory: performance of PBE, SCAN, and HSE06 functionals, *Electron. Struct.* **3**, 027001 (2021).
- [27] R. Schier, H.-D. Saßnick, and C. Cocchi, Stability and electronic properties of CsK₂Sb surface facets, *Phys. Rev. Mater.* **6**, 125001 (2022).
- [28] R. Wu and A. M. Ganose, Relativistic electronic structure and photovoltaic performance of K₂CsSb, *J. Mater. Chem. A* **11**, 21636 (2023).

- [29] R. Schier, D. Guo, H.-D. Saßnick, and C. Cocchi, Stability and electronic properties of K-Sb and Na-Sb binary crystals from high-throughput *ab initio* calculations, *Adv. Theory Simul.* **7**, 2400680 (2024).
- [30] J. Santana-Andreo, H.-D. Saßnick, and C. Cocchi, Thermodynamic stability and vibrational properties of multi-alkali antimonides, *JPhys Mater.* **7**, 035004 (2024).
- [31] G. Wang, J. Zhang, C. Huang, D. A. Dimitrov, A. Alexander, and E. I. Simakov, First-principles study of structural, elastic, electronic, transport properties, and dielectric breakdown of Cs₂Te photocathode, *Sci. Rep.* **15**, 2780 (2025).
- [32] C. Xu, R. Schier, and C. Cocchi, Electronic and optical properties of computationally predicted Na-K-Sb crystals, *Electron. Struct.* **7**, 015001 (2025).
- [33] G. F. Bertsch, J.-I. Iwata, A. Rubio, and K. Yabana, Real-space, real-time method for the dielectric function, *Phys. Rev. B* **62**, 7998 (2000).
- [34] N. T. Maitra, Perspective: Fundamental aspects of time-dependent density functional theory, *J. Chem. Phys.* **144**, 220901 (2016).
- [35] K. Yabana and G. Bertsch, Time-dependent local-density approximation in real time: application to conjugated molecules, *Int. J. Quantum Chem.* **75**, 55 (1999).
- [36] T. Otake, M. Yamagiwa, J.-I. Iwata, K. Yabana, T. Nakatsukasa, and G. F. Bertsch, First-principles electron dynamics simulation for optical breakdown of dielectrics under an intense laser field, *Phys. Rev. B* **77**, 165104 (2008).
- [37] X. Zhang, F. Wang, Z. Liu, X. Feng, and S. Pang, Controlling energy transfer from intense ultrashort light pulse to crystals: A comparison study in attosecond and femtosecond regimes, *Phys. Lett. A* **384**, 126710 (2020).
- [38] A. M. Cabrera, M. Guerrini, H. P. Pinto, and C. Cocchi, Ultrafast charge carrier dynamics of methylammonium lead iodide from first principles, *Electron. Struct.* **6**, 037001 (2024).
- [39] C. Wang, L. Jiang, F. Wang, X. Li, Y. Yuan, H. Xiao, H.-L. Tsai, and Y. Lu, First-principles electron dynamics control simulation of diamond under femtosecond laser pulse train irradiation, *J. Phys.: Condens. Matter* **24**, 275801 (2012).
- [40] X. Kong, F. Wang, X. Zhang, Z. Liu, and X. Wang, Dielectric properties of cubic boron nitride modulated by an ultrashort laser pulse, *Phys. Rev. A* **98**, 053439 (2018).
- [41] G. Su, F. Wang, L. Jiang, X. Zhang, X. Su, L. Qu, and Y. Lu, Ultrafast response of dielectric properties of monolayer phosphorene to femtosecond laser, *J. Appl. Phys.* **121**, 173105 (2017).
- [42] N. Tancogne-Dejean and A. Rubio, Atomic-like high-harmonic generation from two-dimensional materials, *Sci. Adv.* **4**, eaao5207 (2018).
- [43] M. Uemoto, S. Kurata, N. Kawaguchi, and K. Yabana, First-principles study of ultrafast and nonlinear optical properties of graphite thin films, *Phys. Rev. B* **103**, 085433 (2021).
- [44] J. Zhang, H. Hong, C. Lian, W. Ma, X. Xu, X. Zhou, H. Fu, K. Liu, and S. Meng, Interlayer-state-coupling dependent ultrafast charge transfer in MoS₂/WS₂ bilayers, *Adv. Sci. (Weinheim, Ger.)* **4**, 1700086 (2017).
- [45] K. Iida, M. Noda, and K. Nobusada, Photoinduced electron transfer at the interface between heterogeneous two-dimensional layered materials, *J. Phys. Chem. C* **122**, 21651 (2018).
- [46] M. Jacobs, J. Krumland, and C. Cocchi, Laser-controlled charge transfer in a two-dimensional organic/inorganic optical coherent nanojunction, *ACS Appl. Nano Mater.* **5**, 5187 (2022).
- [47] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [48] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [49] K. Yabana and G. F. Bertsch, Time-dependent local-density approximation in real time, *Phys. Rev. B* **54**, 4484 (1996).
- [50] N. Tancogne-Dejean, M. J. T. Oliveira, X. Andrade, H. Appel, C. H. Borca, G. Le Breton, F. Buchholz, A. Castro, S. Corni, A. A. Correa, U. De Giovannini, A. Delgado, F. G. Eich, J. Flick, G. Gil, A. Gomez, N. Helbig, H. Hübener, R. Jestädt, J. Jorner-Somoza *et al.*, Octopus, a computational framework for exploring light-driven phenomena and quantum dynamics in extended and finite systems, *J. Chem. Phys.* **152**, 124119 (2020).
- [51] K. Yabana, T. Nakatsukasa, J.-I. Iwata, and G. Bertsch, Real-time, real-space implementation of the linear response time-dependent density-functional theory, *Phys. Status Solidi B* **243**, 1121 (2006).
- [52] E. Runge and E. K. U. Gross, Density-functional theory for time-dependent systems, *Phys. Rev. Lett.* **52**, 997 (1984).
- [53] Y.-T. Chang and Y.-H. Chan, Diagrammatic approach to excitonic effects on nonlinear optical response, *Phys. Rev. B* **109**, 155437 (2024).
- [54] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [55] M. Schlupf and F. Gygi, Optimization algorithm for the generation of ONCV pseudopotentials, *Comput. Phys. Commun.* **196**, 36 (2015).
- [56] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [57] A. Yamada and K. Yabana, Multiscale time-dependent density functional theory for a unified description of ultrafast dynamics: Pulsed light, electron, and lattice motions in crystalline solids, *Phys. Rev. B* **99**, 245103 (2019).
- [58] S.-H. Wei and A. Zunger, Electronic structure of M₂Sb-type filled tetrahedral semiconductors, *Phys. Rev. B* **35**, 3952 (1987).
- [59] K. Jack, M. Wachtel, and W. Bragg, The characterization and crystal structure of caesium antimonide, a photo-electric surface material, *Proc. R. Soc. London, Ser. A* **239**, 46 (1957).
- [60] G.-X. Zhang, A. M. Reilly, A. Tkatchenko, and M. Scheffler, Performance of various density-functional approximations for cohesive properties of 64 bulk solids, *New J. Phys.* **20**, 063020 (2018).
- [61] I. Schewe-Miller and P. Böttcher, Synthesis and crystal structures of K₅Se₃, Cs₅Te₃ and Cs₂Te, *Z. Kristallogr.* **196**, 137 (1991).
- [62] H.-D. Saßnick and C. Cocchi, Exploring cesium-tellurium phase space via high-throughput calculations beyond semi-local density-functional theory, *J. Chem. Phys.* **156**, 104108 (2022).
- [63] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/449c-nn6y> for additional information on the electronic properties and nonlinear response of Cs₃Sb and Cs₂Te.
- [64] K. Momma and F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* **44**, 1272 (2011).

- [65] C. Vorwerk, B. Aurich, C. Cocchi, and C. Draxl, Bethe–Salpeter equation for absorption and scattering spectroscopy: Implementation in the exciting code, *Electron. Struct.* **1**, 037001 (2019).
- [66] D. Golde, T. Meier, and S. W. Koch, High harmonics generated in semiconductor nanostructures by the coupled dynamics of optical inter- and intraband excitations, *Phys. Rev. B* **77**, 075330 (2008).
- [67] G. Vampa, C. R. McDonald, G. Orlando, D. D. Klug, P. B. Corkum, and T. Brabec, Theoretical analysis of high-harmonic generation in solids, *Phys. Rev. Lett.* **113**, 073901 (2014).
- [68] T. A. Driscoll and D. Guidotti, Symmetry analysis of second-harmonic generation in silicon, *Phys. Rev. B* **28**, 1171 (1983).
- [69] N. Tancogne-Dejean, O. D. Mücke, F. X. Kärtner, and A. Rubio, Impact of the electronic band structure in high-harmonic generation spectra of solids, *Phys. Rev. Lett.* **118**, 087403 (2017).
- [70] Y. Jiao, F. Wang, X. Hong, W. Su, Q. Chen, and F. Zhang, Electron dynamics in CaB_6 induced by one- and two-color femtosecond laser, *Phys. Lett. A* **377**, 823 (2013).
- [71] G. Wachter, C. Lemell, J. Burgdörfer, S. A. Sato, X.-M. Tong, and K. Yabana, *Ab initio* simulation of electrical currents induced by ultrafast laser excitation of dielectric materials, *Phys. Rev. Lett.* **113**, 087401 (2014).
- [72] H. Qi, J. Wang, Z. Xu, and F. Fang, First-principles study of electron dynamics of MoS_2 under femtosecond laser irradiation from deep ultraviolet to near-infrared wavelengths, *J. Chem. Phys.* **161**, 224709 (2024).
- [73] H. Bellersen, M. Guerrini, and C. Cocchi (2025), <https://doi.org/10.5281/zenodo.15005277>