Anisotropic high-harmonic generation in bulk crystals

1. Semi-classical electron trajectory calculations in MgO crystal

In the main text, we use a semi-classical model to describe the electron motion inside MgO crystal. In this model, the equation of motion of electron under laser field \( E(t) = E_0 \cos(\omega t) \) (\( \omega \): drive-laser frequency) is given by

\[ \frac{dk}{dt} = -\frac{aE(k)}{\hbar} \]

where \( k \) is the crystal momentum. The time evolution of the position of an electron wavepacket \( r \) can be solved by

\[ \frac{dr}{dt} = -\frac{\partial E(r)}{\partial k} \]

where \( E(k) \) is the energy dispersion of the conduction band. Here, the energy dispersion \( E(k) \) (in eV) in (001) plane is approximated by a tight-binding model for a face-center cubic (FCC) crystal,

\[ E(k_x k_y k_z = 0) = 3(A + B) - A (\cos \frac{k_x a}{2} + \cos \frac{k_y a}{2} + \cos \frac{k_z a}{2} - \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} - B(1 + \cos k_x a + \cos k_y a), \]

where \( A=1.25 \) and \( B=0.6 \) is used to fit with the structure reported by Tan et al. Figures S1a and S1b show the 2-D conduction band in the polarization plane and 1D cuts along the high symmetry directions respectively.

![Figure S1](image1.png)

**Figure S1** | a, Conduction band structure in 2-D, The dispersion along \( \Gamma-K \) and \( \Gamma-X \) is shown in b. For comparison, dotted red line shows a parabolic band. (a.u.: atomic units)

First, we show electron trajectories in one dimension in the real-space considering the MgO band along \( \Gamma-X \) direction. For comparison, we also plot trajectories using a free-electron-like parabolic band in the effective mass approximation. We find that under relatively moderate field (Fig. S2a, \( E_0=0.1 \) V/A, dotted line), the electron excursion amplitudes for the non-parabolic band and the parabolic band are almost identical throughout the laser cycle. However, at sufficiently high fields such as \( E_0=1 \) V/A, the trajectories begin to differ especially for relatively longer propagation time (for example at \( \pi \) phase) as it is seen in Fig S2b.

![Figure S2](image2.png)

**Figure S2** | Electron dynamics in conduction band under field strength of (a) 0.1 V/A and (b) 1 V/A. The distance is shown in units of lattice constant (\( a=4.2 \) Å). (a.u.: atomic units. p: parabolic band; np: non-parabolic band along \( \Gamma-X \))
2. Electron trajectories in two-dimension

We calculate the trajectories in two-dimension in MgO under linear and elliptical polarization. In the linear case, trajectories in Fig. 3 of the main text is calculated under electric field \( E(t) = E_0 \cos(\omega t)(\cos \theta \hat{y} + \sin \theta \hat{x}) \), where \( \omega \) is the laser frequency and \( \theta \) is the polarization angle of laser relative to a cubic axis. For elliptical light calculation in Fig 4 and 5 of main text, trajectories are calculated under electric field of \( E(t) = E_0 \cos(\omega t) \hat{y} + E_x \sin(\omega t) \hat{x} \), where \( \epsilon = E_x/E_y \) defines the ellipticity. We consider the initial phase of 0.1 \( \pi \), which would correspond to the emission phase of highest harmonic in the atomic case, and show propagation up to 0.50 \( \pi \).

Here, we compare electron trajectories in parabolic and non-parabolic band. First, we look at the case of linear polarization, similar to the conditions in Fig. 3 of the main text. Fig S3a shows the trajectories when the field is along \( \theta = 0, 12, 45, 78 \) and 90°. Next, we investigate the case for elliptical polarization, with a representative ellipticity, \( \epsilon = 0.4 \) and major polarization axis is aligned with Mg-O bonding direction in the crystal. The trajectories are shown in Fig S3b. For short time scales (the propagation time of 0.2 of laser period) the trajectories in parabolic and non-parabolic band are similar to each other.

![Figure S3](image)

**Figure S3** | **a**, Electron trajectories in MgO with parabolic (dotted) and non-parabolic band (solid) under linearly polarized light at field strength of 1.0 V/Å. **b**, Electron trajectories in MgO under elliptical light (\( \epsilon = 0.4 \)) with parabolic (dotted) and non-parabolic band (solid).

3. Electron and hole dynamics in two dimensions

Next, we look at both electron and hole dynamics in two-dimension in the real-space. Similar to the energy dispersion of the conduction band in section 1, the energy dispersion of valence band follows the same expression with \( A = -0.25 \) and \( B = 0 \). Figure S3a shows the 2-D valence band in the polarization plane. We consider the case of elliptical polarization and crystal is rotated such that crystal axis sets 15° with the major polarization axis. Peak field is 1V/Å and \( \epsilon = 0.2 \). Electron and hole trajectories are shown from various initial phase -0.1, 0 and 0.1 \( \pi \) to final phase of 2.5 \( \pi \) (see Fig. S4). In all cases, it is seen that the electron and hole travel away from each other. Thus it is suggestive that same site re-collision is not possible when the laser field is elliptically polarized. We note that the generalized recollision model discussed recently by Vampa *et al.* requires that an electron and its associated hole from the same site meet spatially in order to recombine and produce harmonic photons. The trajectory analysis shows that such re-combination is strongly suppressed in a highly elliptical field because of the relative transverse motion of the electron and hole. Since we measure harmonic signal in the experiment, we conclude that harmonic generation process must involve multiple atomic sites in the crystal.
4. Angular distribution of HHG signal

Although semi-classical electron trajectory analysis method does not provide harmonic yield quantitatively, it is able to predict angular distribution for a known crystal structure. Because of the brief nature of the HHG process, it is a reasonable to assume that the lattice remains fully intact without any structural changes, therefore we use parameters of the MgO crystal from the literature. In our analysis, we assume that harmonic yield depends on the closeness of the electron trajectories with respect to the ion cores in the crystal. For illustrative purposes, we take a Gaussian distribution of the charge density around the cores, such that the harmonics yield \( I_{\text{HHG}} \), can be expressed as

\[
I_{\text{HHG}} \propto C_{\text{mg}} e^{-\frac{(r-r_{\text{mg}})^2}{2a_{\text{mg}}^2}} + C_{\text{o}} e^{-\frac{(r-r_{\text{o}})^2}{2a_{\text{o}}^2}}
\]

where \( r \) is the closest distance of the electron with the center of atomic core, \( r_{\text{mg}} \) and \( r_{\text{o}} \) is the location of magnesium and oxygen ionic core, \( a_{\text{mg}} \) and \( a_{\text{o}} \) are the size of the ionic core, and \( C_{\text{mg}} \) and \( C_{\text{o}} \) correspond to strength of harmonics for collisions at magnesium and oxygen respectively. In our calculation, \( a_{\text{o}} = 0.35a \) and \( a_{\text{mg}} = 0.1a \) (\( a \): lattice constant), taken from reference\(^3\) and \( C_{\text{mg}} = 1, C_{\text{o}} = 0.15 \) are chosen to match the relative maxima along the Mg-O and O-O directions for the 21st harmonics. Figure S5 shows the comparison of the experimental yield of 21st harmonic (red dots) with calculated results (blue line, scaled to match experimental magnitude); the calculation reproduces well the anisotropy observed in experiment.

Figure S5 a, Trajectories under various linear polarizations. b, Harmonics yield of 21st harmonics from experiment (red dot) and simulation (blue line).
Reference

