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1 **Attosecond spectral singularities in solid-state**
2 **high-harmonic generation**

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22 **Strong field driven electric currents in condensed matter systems open**
23 **new frontiers in petahertz electronics. In this regime new challenges arise**
24 **as the role of the band structure and the quantum nature of electron-hole**
25 **dynamics have yet to be resolved. Here we reveal the underlying attosec-**
26 **ond dynamics that dictates the temporal evolution of carriers in multi-band**
27 **solid state systems, via high harmonic generation (HHG) spectroscopy. We**
28 **demonstrate that when the electron-hole relative velocity approaches zero,**
29 **enhanced quantum interference leads to the appearance of spectral caustics**
30 **in the HHG spectrum. Introducing the role of the dynamical joint density**
31 **of states (JDOS) we identify its direct mapping into the spectrum, exhibit-**
32 **ing singularities at the spectral caustics. By probing these singularities, we**
33 **visualize the structure of multiple unpopulated high conduction bands. Our**
34 **results open a new path in the control and study of attosecond quasi-particle**
35 **interactions within the field dressed band structure of crystals.**

36 Induced by the strong field interaction, HHG provides a unique spectroscopic
37 scheme to visualize the coherent evolution of petahertz currents inside solids.
38 Since the first observation [1], solid HHG opened a door into the study of the
39 electronic structure and dynamics in crystals [2, 3, 4, 5, 6, 7], multiple band dy-
40 namics [8, 9, 10, 11] and complex many-body phenomena [12] in crystalline and
41 amorphous systems [9]. For a moderate field strength the electron-hole dynamics
42 are often described semi-classically by a single valence and conduction band of

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43 the crystal. As we approach the strong field regime, new fundamental questions
44 arise. What is the role of the band structure in such intense, ultrafast processes?
45 How will electrons and holes interact on extremely short time scales, when they
46 are still mutually quantum coherent? These questions pose some of the primary
47 challenges in the emerging field of strong field interactions in solids.

48 In this paper we identify the quantum nature of the electron-hole wave-packet
49 in solids, probing its strong-field attosecond dynamics over multiple bands. We
50 observe enhanced quantum interference in the vicinity of Van Hove singularities
51 [13, 14] and resolve the direct link between the dynamical JDOS and the HHG
52 spectrum. Our study applies HHG spectroscopy in MgO, induced by a $\lambda = 1.3\mu m$
53 driving laser field. Adding a weak perturbative second harmonic (SH) field mod-
54 ulates the internal dynamics, in a close analogy to a lock-in measurement. This
55 scheme allows us to isolate extremely weak signals and identify the contribution
56 of multiple band excitations, covering a spectral range of up to 30 eV. Our results
57 show unequivocally that the internal dynamics related to HHG are dominated by
58 the interband emission [1, 3, 4, 7, 15, 16, 17, 18, 19, 20, 21], which remains the
59 dominant mechanism even when higher conduction bands are involved. We iden-
60 tify the mapping between the dynamical JDOS at unique regions in the Brillouin
61 zone (BZ) and the HHG spectrum. At Van Hove singularities, spectral caustics
62 are induced, leading to a strong enhancement of the HHG signal. At these criti-
63 cal points, the semi-classical picture fails [22], imprinting the dynamical quantum
64 nature of the strong field interaction on the HHG spectrum.

65 The interband HHG mechanism can be viewed as a generalized electron-hole
66 recollision process [15, 19], described by a semi-classical analysis [22]. Around

67 the peak of the laser field, an electron tunnels from the valence to the conduction
68 band, forming an electron-hole pair. The laser field subsequently accelerates the
69 pair, leading to their recombination and the emission of XUV radiation. This
70 recollision model maps the semi-classical electron-hole trajectories into harmonic
71 energies. The semi-classical analysis is not strictly limited to one conduction band
72 – the strong laser field may excite the electron into higher bands, leading to the
73 generation of complex spectral features in the HHG spectrum [8, 9, 10].

74 A fundamental aspect of strong-field induced tunneling is the localization of
75 the excited electron-hole wave-packet in the BZ around the minimum band gap.
76 As the wave-packet evolves under the influence of the laser field, it dynamically
77 probes a narrow stripe of the BZ along the field’s polarization, as illustrated in
78 figure 1e. Such localization is a key property of HHG spectroscopy – enabling the
79 visualization of the band structure with unique angular resolution.

80 Resolving the angular dependence of the HHG spectrum is extremely chal-
81 lenging – the HHG signal drops rapidly when the polarization is rotated off the
82 main axes of the MgO crystal [23]. Such suppression becomes even more sig-
83 nificant when the harmonics are produced from higher conduction bands [24]. In
84 order to fully reveal the electron-hole dynamics, both its angular dependence as
85 well as the contribution of multiple bands, we introduce an advanced measure-
86 ment scheme that enables us to resolve and isolate the weak HHG signals.

87 Enhancing the detectability of weak signals by subjecting them to a known
88 temporal modulation is a common practice in a wide range of applications, also
89 known as lock-in measurement. We induce such a modulation by adding a weak
90 SH field polarized perpendicular to the fundamental field’s polarization. So far

91 this scheme has been applied to probe the internal dynamics in gas phase HHG
92 [25] (and references within) and interband currents in ZnO [15]. Scanning the
93 two-color delay leads to a periodic modulation of the HHG spectrum with four
94 times the fundamental laser's frequency. Fourier analysis isolates the oscillating
95 component, resolving the extremely weak HHG signals, buried in a large exper-
96 imental background. In addition, XUV emission from higher conduction bands
97 can be highly susceptible to the two-color delay [26], resulting in an enhanced
98 signature in the oscillating component. Figures 1a, 1b and 1c compare the Fourier
99 amplitudes of the modulated HHG signals and the spectra averaged over the two
100 color delay for crystal orientations of 0° , 33° and 45° , respectively (see figure 1d).
101 Clearly, the averaged spectrum is accompanied by large background noise and is
102 dominated by harmonic 17 (~ 16.2 eV) for 33° and 45° and harmonics 17 and 19
103 (~ 18.1 eV) for 0° . Resolving the oscillating spectrum by Fourier analysis shows a
104 dramatic enhancement of the signal over the noise. This measurement exhibits the
105 appearance of new spectral components, which were so far hidden in the averaged
106 spectrum.

107 The oscillating spectra reveal that for all crystal angles, the spectrum extends
108 beyond the first band edge (~ 18 eV), indicating the strong contribution of higher
109 conduction bands. The most important observation is associated with the angular
110 dependence of the measurement – the oscillating spectrum varies drastically and
111 surprisingly for different angles exhibiting enhanced features and structures over
112 a wide spectral range. We identify three distinct structures: enhanced harmonics
113 around 16-17 eV extending to 18 eV at 0° , an increased signal in the 20.5-22.5 eV
114 region at 33° and a clear spectral feature at 23.5-26 eV, narrowing at 45° . These

115 features can not be associated with the spectral response of the dipole coupling
 116 between the bands, due to their moderate variation with energy (see SI). What
 117 is the origin of the enhancement mechanism in these spectral regions and what
 118 information does it provide?

119 We start by analyzing the enhancement at 23.5-26 eV. This observation is strik-
 120 ing – clearly, this spectral region originates from a high conduction band excitation
 121 associated with a low population transfer. Furthermore, while the oscillating spec-
 122 trum changes dramatically with the crystal orientation, this feature remains robust.
 123 Such observation suggests that it originates from areas of the BZ which are orien-
 124 tation independent. These areas can be found around the Γ point of the BZ which
 125 is common to all crystal orientations. Figures 2a and 2b describe the band struc-
 126 ture for crystal orientations of 0° and 45° , respectively. Indeed, we find two high
 127 conduction bands intersecting the Γ point at an energy of 24.57 eV. At the Γ point
 128 these bands, as well as any band, have a critical point, $\nabla_{\mathbf{k}}E_c(\mathbf{k}) = \nabla_{\mathbf{k}}E_v(\mathbf{k}) = 0$,
 129 such that the gradient of the energy gap is zero as well:

$$\nabla_{\mathbf{k}}(E_c(\mathbf{k}) - E_v(\mathbf{k})) = \nabla_{\mathbf{k}}\varepsilon_g(\mathbf{k}) = 0 \quad (1)$$

130 where \mathbf{k} is the lattice momentum, E_c is the conduction band and E_v is the va-
 131 lence band. At the critical points, where $\nabla_{\mathbf{k}}\varepsilon_g(\mathbf{k}) = 0$, the JDOS of a crystalline
 132 solid becomes singular. These singularities are known as Van Hove singulari-
 133 ties and most commonly arise in the analysis of optical absorption and reflection
 134 spectra [27, 28]. In contrast to these measurements, performed over long time
 135 scales, HHG in bulk crystal is attributed to the sub-cycle electronic dynamics
 136 where the electron and hole wave-packets remain mutually coherent. In addition,

137 these wave-packets, which are initiated by tunneling, are localized in the BZ. As
 138 a result, the harmonic emission can not be understood by merely counting the
 139 total number of available states throughout the BZ. Instead, the quantum nature
 140 of the singularity has to be considered at specific \mathbf{k} regions. During such short
 141 time scales, we can view the singularities as points where the relative velocity of
 142 the electron and hole wave-packets is zero. This results in enhanced interference
 143 effects, encoding dynamical quantum information into the HHG spectrum.

144 The quantum expression for the interband currents can be written as [19, 22]

$$\mathbf{j}_{er}(\omega) = \omega \int_{B.Z.} d^3\mathbf{k} \iint \mathbf{g}(\mathbf{k}, t', t) \exp^{-iS(\mathbf{k}, t', t) + i\omega t} dt dt' \quad (2)$$

$$S(\mathbf{k}, t', t) = \int_{t'}^t \varepsilon_g(\mathbf{k} - \mathbf{A}(t) + \mathbf{A}(\tau)) d\tau \quad (3)$$

145 where \mathbf{A} is the vector potential and ω the harmonic energy. $g(\mathbf{k}, t', t)$ represents
 146 the slowly varying term compared to the fast oscillating exponential containing
 147 the semi-classical action, $S(\mathbf{k}, t', t)$. Under these conditions we can use the sta-
 148 tionary phase approximation (SPA) for $\mathbf{j}_{er}(\omega)$ which defines the semi-classical
 149 mapping between harmonic energy and recolliding electron and hole trajectories.
 150 The interband current for a single stationary solution as obtained from the SPA, is
 151 proportional to $\sqrt{|\hat{\mathbf{S}}''(\mathbf{k}_{st}, t'_{st}, t_{st})|^{-1}}$, where $\hat{\mathbf{S}}''(\mathbf{k}_{st}, t'_{st}, t_{st})$ is the Hessian matrix
 152 of the function $S(\mathbf{k}, t', t)$ at the stationary points. This derivation directly links the
 153 HHG spectrum and the band structure (for a detailed derivation see SI):

$$I(\omega) \propto |\mathbf{j}_{er}(\omega)|^2 \propto \omega^2 \left| \sum_{\mathbf{k}_{st}} \frac{\tilde{\mathbf{g}}(\mathbf{k}_{st}, t'_{st}, t_{st}) e^{-iS(\mathbf{k}_{st}, t'_{st}, t_{st})}}{\sqrt{|\nabla_{\mathbf{k}} \varepsilon_g(\mathbf{k}_{st})|}} \right|^2 \quad (4)$$

154 where $\varepsilon_g(\mathbf{k}_{st})$ is the energy difference between electron and hole at the time of rec-
 155 ollision, which defines the harmonic energy, and $\tilde{\mathbf{g}}$ accounts for all pre-exponential
 156 terms. The expression for the spectral intensity strongly resembles that of the
 157 JDOS, except it is weighted by the exponent of the semi-classical action, there-
 158 fore, it is associated with a *dynamical JDOS*. This exponent gives the quantum
 159 phase and amplitude associated with each trajectory. Due to strong field tunnel-
 160 ing, the quantum amplitude strongly attenuates with increasing $|\mathbf{k}_{st}^\perp|$, \mathbf{k}_{st}^\perp being
 161 the component of \mathbf{k}_{st} perpendicular to the laser's polarization. Such attenuation
 162 expresses the fact that HHG indeed originates from a narrow stripe of the BZ, pro-
 163 viding the significant angular dependence of the spectrum. Clearly this mapping
 164 becomes singular at the extrema of the energy gap as described by equation (1).

165 The singularity in the mapping between harmonic energy and electron-hole
 166 trajectories can be described within the framework of caustics [29]. Caustics
 167 are universal phenomena in nature that link processes observed in many differ-
 168 ent branches of physics. Previous studies identified the appearance of caustics in
 169 gas phase HHG [29, 30], where they reveal the quantum nature of the process in
 170 a regime where classical analysis fails. Figure 1e illustrates the origin of spec-
 171 tral caustics in condensed matter systems, when the electron-hole wave-packet
 172 has zero relative velocity at the extrema of the band gap. We find that spectral
 173 caustics reveal the rich, quantum, spatio-temporal nature of electronic dynamics
 174 in solids, dictated by the direct link between the band structure and strong field
 175 interaction.

176 The enhancement at 23.5-26 eV can be identified as a spectral caustic orig-
 177 inating from the Γ point. Figures 2a, 2d present the band structure for crystal

178 orientations of 0° and 45° , respectively. Another energy band intersecting the Γ
 179 point can be found at 18.8 eV (figure 2d), leading to a robust spectral feature near
 180 18 eV as can be seen in figures 1a-c. While the crossing of energy bands at the
 181 Γ point will always result in singularities, spectral caustics can be found at other
 182 points in the BZ as well. Along the high symmetry axes of the crystal, 0° and
 183 45° , each band-gap consists of several critical points where $\nabla_{\mathbf{k}}\varepsilon_g(\mathbf{k}_{st}) = 0$. In
 184 figure 2 we show how these points are directly imprinted in the experimentally
 185 resolved HHG spectrum. Figures 2b, 2e describe the gradient of each band gap as
 186 a function of the band gap energy, for crystal orientations of 0° and 45° , respec-
 187 tively. Figures 2c, 2f present the measured oscillating spectra at these angles. The
 188 highlighted lines in figures 2c, 2f emphasize the energy points where the gradi-
 189 ent is zero and the dynamical JDOS becomes singular according to equation (4) .
 190 Indeed, caustics dominate the brightest features in the HHG spectrum, leading to
 191 a dramatic spectral focusing and enhancement of the weak signal associated with
 192 higher conduction bands excitation.

193 While the singularities are observed along the high symmetry axes of the crys-
 194 tal, figure 3a shows that enhanced spectral features are observed at other angles
 195 as well . Their origin can be understood through the dynamical JDOS, by looking
 196 at the gradient of the different band gaps, $\nabla_{\mathbf{k}}\varepsilon_g(\mathbf{k})$. Figures 3b and 3c present
 197 2D images of the gradients of bands 5 and 7. In both bands we can identify a
 198 pronounced valley at specific \mathbf{k} values and across a large angular range. Along
 199 these valleys $\nabla_{\mathbf{k}}\varepsilon_g(\mathbf{k})$ is small, leading, according to equation (4) to a local spec-
 200 tral enhancement in the HHG signal. Specifically, the gradient valley at band 5
 201 is mapped to a pronounced spectral enhancement around 16-17 eV, while the val-

202 ley in band 7 leads to the enhanced spectral feature in the 20.5-22.5 eV region,
203 marked by the violet and cyan areas, respectively. Importantly, their observation
204 is robust with the crystal orientation, mapping the angular variation of the gradient
205 valleys.

206 Understanding the mapping between the band structure and the HHG spectrum
207 allows us to study the fundamental dynamical properties of strong field dressed
208 phenomena in solids [11, 31]. Such effects play an important role when the band
209 structure becomes degenerate. In the vicinity of these regions the intricate inter-
210 play between the strong field dressing and the orientation dependent band cou-
211 plings can have a dramatic effect on the electronic dynamics. At the Γ point of
212 MgO there is a two band degeneracy at 24.6 eV (bands 9 and 10, plotted in green
213 and in red), protected by the crystal symmetries. Taking a closer look at the asso-
214 ciated caustic we find that our measurement encodes a signature of such a strong
215 field mechanism. The enhancement observed at the high energy end of the spec-
216 trum, 23.5-26 eV, is robust with crystal orientation, as one would expect from a
217 feature originating from the Γ point. However, the spectral shape of this feature
218 shows a striking angular dependence, where the peak shifts from harmonic 25 at
219 0° to 26 at 45° , exhibiting complex spectral structures at intermediate angles (see
220 dashed line in figure 3a). By rotating the crystal we change the couplings and
221 field dressing of these two bands, imprinting the intricate underlying strong field
222 dynamics into the angular dependence of the HHG spectrum.

223 Our results establish the fundamental connection between the electronic struc-
224 ture of the crystal and the strong field process. This study reveals how strong
225 field attosecond metrology serves as an extremely sensitive probe of ultrafast dy-

226 namical quantum interference between electron-hole wave-packets in solids. We
227 identify the important role of the dynamical JDOS, dictated by the strong field
228 nature of the interaction. As the dynamical JDOS becomes singular, the trajec-
229 tory picture that governs the interband HHG process fails, giving rise to spectral
230 caustics. These findings provide a unique insight into the dressing of the band
231 structure by the strong laser field. The mapping between the HHG spectrum and
232 the band gaps serves as unequivocal evidence to the dominant role of interband
233 emission over numerous conduction bands. Looking forward, our study will form
234 the framework for a large range of attosecond scale phenomena, opening a new
235 path in the study of quasi-particle interactions within the field dressed band struc-
236 ture of crystals. It will allow the study of ultrafast dynamics such as electron-hole
237 interactions, leading to the formation of excitons, or electron-electron-phonon in-
238 teractions. Furthermore, the control over sub-cycle electronic currents will play
239 a role in the establishment of compact solid state XUV sources, as well as in the
240 field of petahertz electronics.

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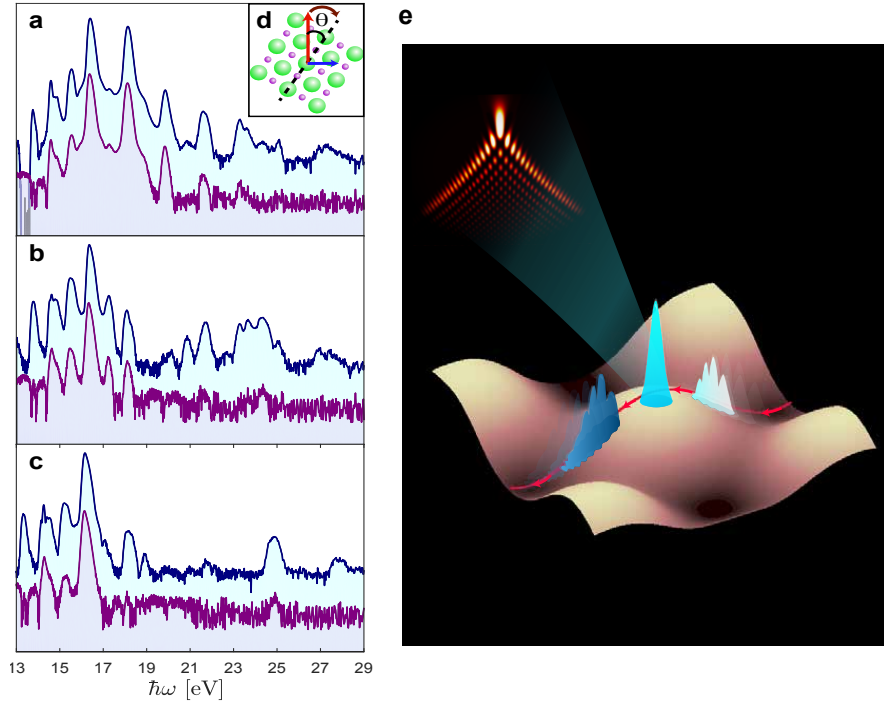


Figure 1: **HHG spectroscopy in MgO.** **a, b, c** normalized oscillating HHG spectrum (cyan) and the normalized averaged spectrum (violet) in logarithmic scale for orientations **a** 0° , **b** 33° and **c** 45° . The two spectra are vertically shifted to allow better visibility. **d** the crystal is oriented to angle θ with respect to the fundamental field's polarization (red arrow) while the second harmonic (blue arrow) is orthogonally polarized. **e** Schematic description of enhanced quantum interference, leading to spectral caustics. The white, cyan and blue wave-packets are snapshots of the combined electron-hole wave-function **at three different times**, probing the band gap of band 10 (figure 2d) along the laser polarization (red line). The modulated white and blue snapshots capture the wave-packet where the electron-hole relative velocity is non-zero. At the extremum of the gap, where the relative velocity is zero (cyan snapshot), enhanced interference leads to the emission of a bright spectral caustic (illustrated by the red interference pattern).

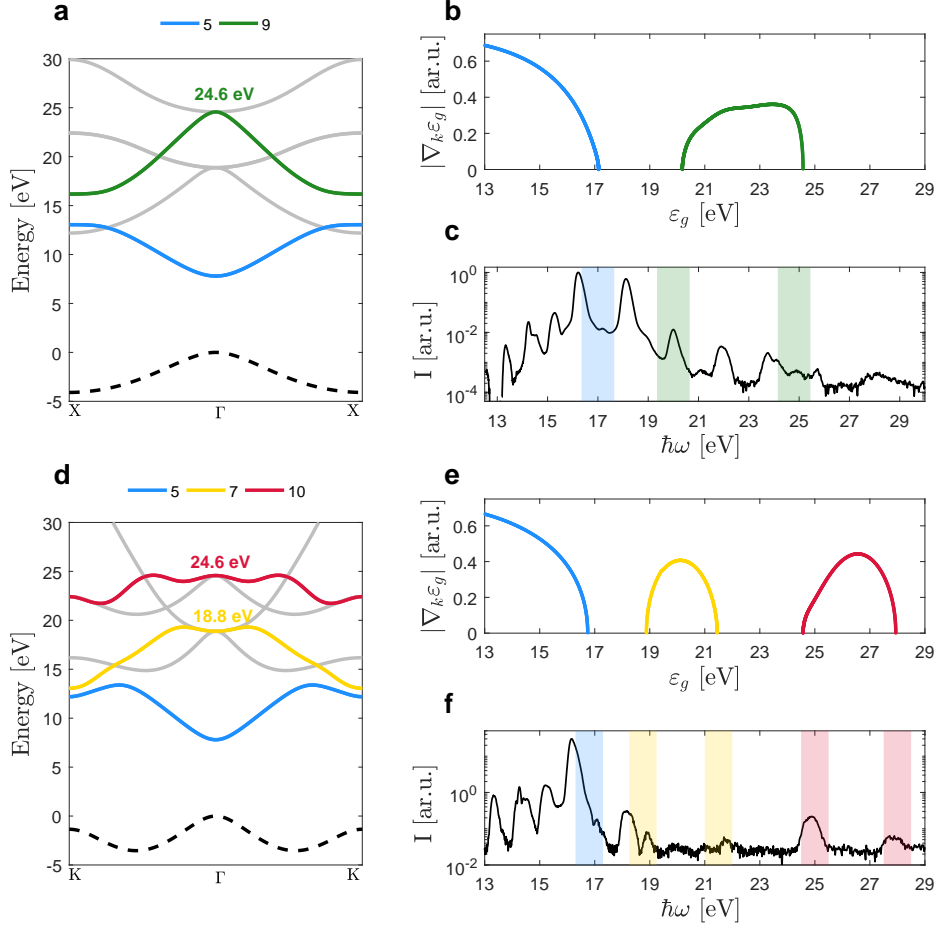


Figure 2: **Spectral caustics at singular points of the dynamical JDOS.** The band structure along the 0° ($\Gamma - X$) (a) and 45° ($\Gamma - K$) (d) orientations, respectively. The dashed line is the valence band and the colored lines are the conduction bands which are dipole coupled to the valence band. The gray bands indicate the existing bands which are not dipole coupled. **b** and **e** plot $|\nabla_{\mathbf{k}} \varepsilon_g(\mathbf{k})|$ along 0° and 45° , respectively. The energies for which $|\nabla_{\mathbf{k}} \varepsilon_g(\mathbf{k})| = 0$, where singularities in the dynamical JDOS occur, are highlighted by corresponding colored bars on the oscillating spectra **c** (0°) and **f** (45°), emphasizing their link to the spectral caustics.

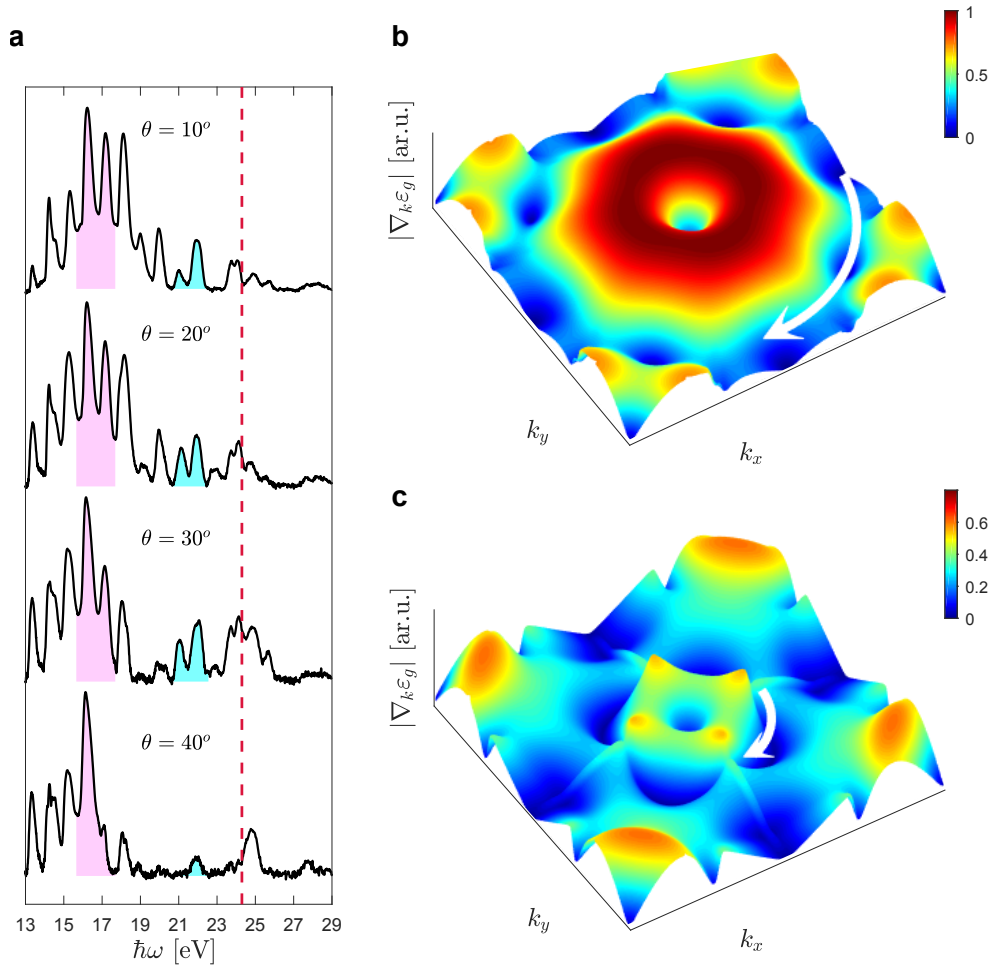


Figure 3: **HHG spectral enhancement at high dynamical JDOS valleys.** **a** the oscillating spectrum for $\theta = 10^\circ, 20^\circ, 30^\circ, 40^\circ$. Two enhanced spectral structures which persist over many orientations are marked by violet and cyan. These spectral structures originate from high dynamical JDOS. The dashed red line marks the spectral caustic between 23.5-26 eV highlighting its angular dependence. **b** and **c** are the 2D gradients of the band gap for bands 5 and 7, respectively. The arrows show valleys of low $|\nabla_{\mathbf{k}}\varepsilon_g(\mathbf{k})|$, i.e. high dynamical JDOS, corresponding to the enhanced spectral features in **a**. The valley in **b** corresponds to the structure marked by violet and **c** to the one in cyan.