Rapid Communications

Observing broken inversion symmetry in solids using two-color high-order harmonic spectroscopy

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We experimentally investigate the manifestations of broken inversion symmetry in solids in two-color interferometric measurements. Polarization-resolved, high-order harmonic spectra of SiO_2 with different levels of crystallinity are obtained. In amorphous and polycrystalline SiO_2, both even and odd harmonics of the two-color interferogram beat four times per fundamental period, which is similar to what was observed in atomic gases or nonoriented molecules. In contrast, when a crystalline SiO_2 sample is utilized, the competition between the contributions of broken inversion symmetries of the medium and the incident electric field results in a distinctive feature: Both odd and even harmonics beat two times per fundamental period [as predicted in Phys. Rev. B **94**, 115164 (2016)]. Our observations are explained by an intuitive model. Moreover, they are fully supported by numerical simulations based on semiclassical transport theory. Our experiments highlight the considerable potential of polarimetry in two-color interferometric measurements, which allow pure and unambiguous characterization of the complex polarization response and thus consequent studies of electron dynamics in solids.

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High-order harmonic generation (HHG) in gases [1,2] using strong-field-driven light-matter interactions has been extensively investigated in the past three decades [3–6]. HHG in gases permitted the study of physical processes that evolve as fast as the natural atomic timescale, which has helped to push the boundary of probing dynamics of matter to the extreme limit: attosecond time resolution and sub-ångström spatial resolution [7–10]. Compared to HHG from gases, HHG from solids is still in its infancy. Ever since the first demonstration of HHG from the bulk of zinc oxide [11], HHG from solids has been a very active field of research with reports of HHG from new crystals as well as different dominant physical mechanisms [12–24].

Symmetry is a powerful concept in science, and it plays an important role in molecular physics and spectroscopy [25,26]. Here, we consider a particularly interesting symmetry property of HHG, which is the emission of even harmonics in the multicycle regime. Upon interacting with multicycle laser pulses, if the medium is inversion symmetric, such as amorphous solids, an atomic gas, or nonoriented molecules, the interaction results in the cancellation of even harmonics, leaving only the odd harmonics in the recorded spectra [1,2]. Hence if the inversion symmetry is broken, either by the medium itself [27–29] or by the incident electric field [30–32], the generation of even harmonics is allowed. This concept has very recently been generalized to the case of bicircular high-order harmonic spectroscopy, which was employed for probing dynamical symmetries of atoms and molecules [33,34].

In solids, two-color HHG has been demonstrated on zinc oxide [17]. However, in all of their measurements, crystalline samples have been used and the measurements were performed using a polarization-integrating spectrometer. Knowing that the crystals with broken inversion symmetry possess a complex polarization response depending on the polarization state of the input laser pulses and how it is aligned with respect to the symmetry axes of the crystal [35,36], we would like to answer the following questions: What is the characteristic difference of two-color interferometry when comparing inversion-symmetric and non-inversion-symmetric solids? Can one reliably extract useful information from two-color measurements using a polarization-integrating spectrometer, or is a polarization-resolved measurement always required? For these purposes, in this Rapid Communication, we performed two-color HHG from SiO_2 of different crystallinities (including α-quartz) in the extreme ultraviolet range of the electromagnetic spectrum. Although we have theoretically anticipated the possible consequence of the competition of broken inversion symmetries in solids, our recent theoretical work [38] implicitly considered linearly polarized fundamental laser pulses as well as their linearly polarized second-harmonic pulses all in the same symmetry plane. It has been shown recently [35] that for α-quartz (and crystals of sixfold symmetry such as GaSe [36]), upon interaction with a linearly polarized fundamental laser pulse along the Γ-K direction, the even harmonics will be parallel to the odd harmonics and to the fundamental laser pulse. When the laser pulse is polarized along the Γ-M direction, the even harmonics will be perpendicular to the odd harmonics [35,36]. This is perfectly reproduced by calculations of the second-order nonlinear susceptibility tensor, described in detail in the Supplemental Material (SM), Sec. II [37]. Considering this fact, we characterize the HHG spectra of two-color interferometry measurements of solids using a polarization-resolving extreme ultraviolet (EUV) spectrometer. The results are fully compatible with the intuitive picture we had proposed in Ref. [38], extended

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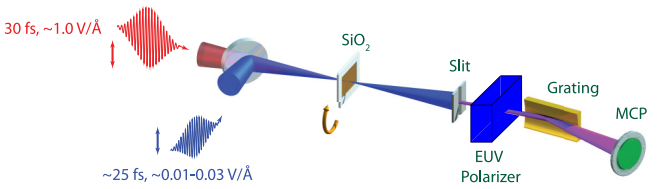

FIG. 1. Experimental apparatus. MCP: Multichannel plate, coupled with a phosphor screen and a CCD camera for fast readout of the HHG spectra. For polarization-integrated measurements, the EUV polarizer is taken out.

to the case of complex polarization states. We also measure the mixed spectra, i.e., using the polarization-integrating spectrometer, and show that their behavior can be explained using semiclassical transport theory. It is important to note that measurements of non-inversion-symmetric samples using a polarization-integrating spectrometer can lead to similar results as the ones obtained from inversion-symmetric samples. Thus one has to be careful while interpreting the two-color data obtained from polarization-integrating measurements.

The experimental setup (Fig. 1) consists of a Mach-Zehnder interferometer for creating a collinear two-color beam. The fundamental beam is linearly polarized with a carrier wavelength of 800 nm and a duration of 30 fs, measured by the transient-grating frequency-resolved optical gating technique [39]. The second-harmonic laser pulses are created by placing a beta-barium borate (BB) in one of the interferometer arms, followed by a $\lambda/2$ wave plate to ensure that the two beams have the same linear polarization. The two collinear beams are then focused on the solid samples, and placed in vacuum to avoid absorption of ultraviolet radiation, at normal incidence. The emitted radiation is recorded downstream using a flat-field grating-based EUV spectrometer. By varying the temporal delay between the fundamental and second-harmonic pulses, we record two-color interferograms for different solid samples, at different crystal orientations.

The recorded, energy-calibrated two-color interferograms for polycrystalline SiO_2 (100 nm) and z-cut α-quartz 20 μm are shown in Fig. 2. We use piecewise normalization to consider only intensity oscillations in the HHG spectra. This additionally removes the effects of peak intensity, band dispersion [15], and Berry curvature [35], focusing only on the specificities of two-color interferometry. For polycrystalline SiO_2 [Fig. 2(a)], both even and odd harmonics beat four times per fundamental period, although the beating amplitude is weaker for odd harmonics. Note that the contrast of the beating amplitude or fringes depends on many parameters, including the spatial overlap and intensity profiles of the two beams, which we do not include in our discussion here. Additionally, we observed that there is virtually no change of the interferogram when the sample is rotated, still residing in the perpendicular plane with respect to the incoming beams. This is identical to the two-color interferogram of fused silica and xenon gas recorded under similar experimental conditions (Fig. SM1 [37]). Our measurement shows that, macroscopically, polycrystalline SiO_2 possesses inversion symmetry.

In contrast, we measure the two-color interferogram of α-quartz in two settings and show the results in Figs. 2(b) and 2(c). The maximum observed photon energy is reduced slightly due to the reflectivity of the polarizer. When the crystal is oriented such that the laser polarization is parallel to the Γ-K direction, the emitted HHG is recorded in parallel polarization, making the first interferogram. The second interferogram is recorded in the Γ-M orientation and perpendicular polarization, respectively. Remarkably, for both cases, almost all odd and even harmonics modulate as a function of time delay, and they beat two times per fundamental period. Furthermore, the intensity modulations of the even harmonics have almost the same phase, which suggests that the dominant emission mechanism is not recollision-based, but intraband excitations [15,16,40].

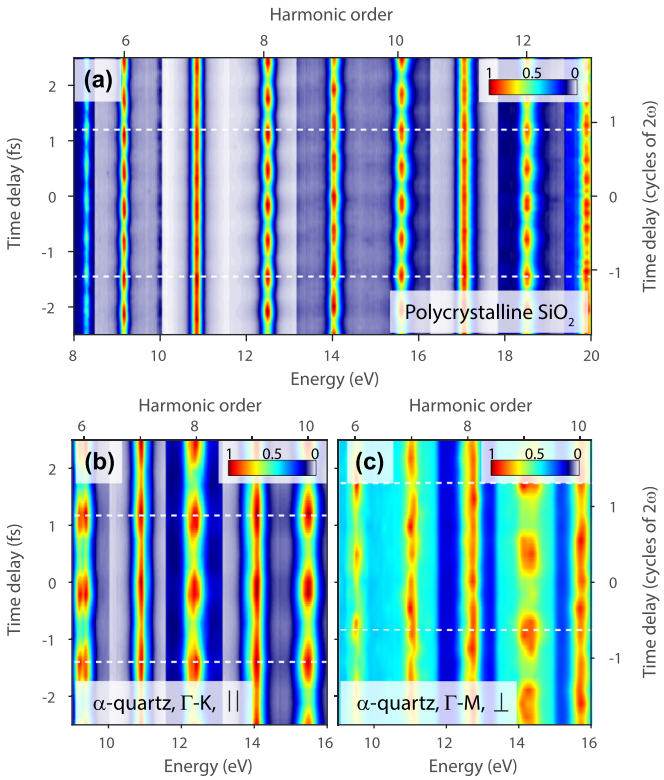

FIG. 2. Distinctive beating patterns in two-color interferometry reveal the complex manifestations of broken inversion symmetry in solids. (a) Measured HHG spectra of polycrystalline SiO_2 as a function of the delay between the fundamental and second-harmonic pulse. The linearly polarized fundamental laser pulse has a pulse duration of 30 fs and a carrier wavelength of 800 nm. (b), (c) Measured HHG spectra of α-quartz as a function of the delay between the fundamental and second-harmonic pulses. The α-quartz sample is oriented such that the incident laser polarization is parallel to the (b) Γ-K and (c) Γ-M directions, respectively. The EUV polarizer is aligned parallel or perpendicular to the polarization direction of the driving field as indicated. The intensity of the second-harmonic pulse is set to 10^{-3} times that of the fundamental pulse. Each harmonic is normalized individually. The delay offsets (absolute phases) are arbitrary. Dashed white lines denote one fundamental laser period.

The distinctive beating patterns of two-color interferograms of SiO_2 can be intuitively explained (see Ref. [38], and Fig. SM4 [37]) and as follows. In an inversion-symmetric medium, a strong, linearly polarized electric field will give rise to an odd-only harmonic spectrum. If we add a weak,

delayed second-harmonic field, this breaks the inversion symmetry and thus enables even-harmonic generation. In the multicycle regime, because the shape of the total electric field repeats after every quarter of the fundamental period, this translates into four beatings per fundamental period of the odd and even harmonics as observed. Since all harmonics are emitted in the same plane, the same observations would be seen, irrespective of whether the EUV spectrometer is polarization integrating or polarization resolving.

For z-cut α-quartz, it is worth considering the input polarization with respect to the symmetry plane of the crystal. The broken inversion symmetry can be represented by a permanent dipole moment in the symmetry plane. When the polarization of the fundamental laser pulses is aligned along the Γ-K direction, the permanent dipole moment creates even harmonics, besides the usual odd harmonics. If we additionally add a second-harmonic field in the same symmetry plane, the competition between broken inversion symmetries results in two beatings per fundamental period, which is observed in Fig. 2(b). When the laser polarization lies along the Γ-M direction, the permanent dipole moment is perpendicular to the laser polarization. The even harmonics generated by the fundamental laser pulses and the permanent dipole will be in the symmetry plane, perpendicular to the odd harmonics. If a weak second-harmonic field is added perpendicular to the symmetry plane, it results in the creation of odd harmonics in the symmetry plane and even harmonics in a plane perpendicular to it, which contains the original odd harmonics (more details in SM, Sec. I [37]). As a result, there are competing even and odd harmonics in both parallel and perpendicular polarizations. The measured two-color interferogram for the perpendicular polarization contains the signature of this competition, hence resulting in two beatings per fundamental period as measured in Fig. 2(c).

In order to support the experimental results and corroborate the intuitive picture of competing broken inversion symmetries, we perform numerical simulations. The same phase of intensity modulations of the even harmonics suggests the use of the semiclassical transport theory [41–43] and it was successfully employed before [15]. In all of the simulations the fundamental electric field is represented according to the measured parameters, and the second-harmonic intensity is set at 3‰ of that of the fundamental pulse although at a relative intensity of $\sim 5 \times 10^{-4}$ the beating patterns can still be observed. The numerical parameters describing the conduction band of SiO_2 are taken from Ref. [44]. Since inversion symmetry is included, the model should be able to emulate the case of fused silica or polycrystalline SiO_2 immediately. Additionally, the broken inversion symmetry can be assigned to quantum interference of different excitation pathways [12] or simply non-inversion-symmetric transition dipole matrix elements between the conduction band and the valence band $\mathbf{D}(\mathbf{k})$ [45]. A simplified way to mimic this feature in the semiclassical theory is to include a non-inversion-symmetric initial electronic wave packet prior to interaction with the driving laser. To account for even-harmonic emission in the perpendicular plane, we employ an extended semiclassical theory where nonvanishing Berry curvature is included [46,47]. The simulation results are shown in Fig. 3 which largely capture the major features of the experimental results (Fig. 2). For

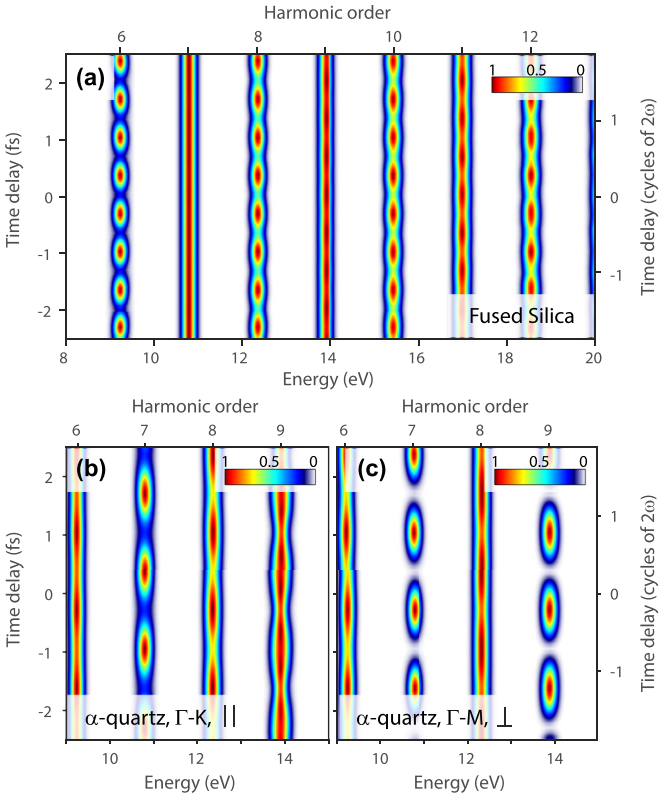

FIG. 3. Complex beating patterns reproduced using semiclassical transport theory. (a) Simulated HHG spectra of fused silica as a function of the delay between the fundamental and second-harmonic pulse. The input is the linearly polarized ultrashort electric field with a pulse duration of 30 fs and a carrier wavelength of 800 nm. (b), (c) Simulated HHG spectra of α-quartz as a function of the delay between the fundamental and second-harmonic pulses. The model mimics the orientation such that the incident laser polarization is parallel to the (b) Γ-K and (c) Γ-M directions, respectively. HHG spectra emitted in parallel and perpendicular directions are shown correspondingly.

fused silica, when no broken inversion symmetry is introduced into the model, it successfully reproduces beatings of both even and odd harmonics four times per fundamental period and the beating amplitude of even harmonics being stronger than that of the odd harmonics. Similar features are captured for the case of α-quartz including two beatings per fundamental period. Due to the fact that the broken inversion symmetry in the Γ-M direction produces even harmonics at the perpendicular polarization and the added second-harmonic field only perturbs it, the even harmonics' amplitude is less modulated in Fig. 3(c). Similarly, because the added second-harmonic field creates new odd harmonics in perpendicular polarization, the new odd harmonics' amplitude is strongly modulated. This is fully compatible with the perturbing picture of inversion symmetric media [32] and Fig. 3(a). In our numerical simulations, because only intraband current is included, the relative phase between odd and even harmonics is constant across the spectrum [16,40]. Moreover, the contrast of the experimentally measured odd harmonics in Fig. 2(c) depends on the Fourier coefficients of the Berry curvature and

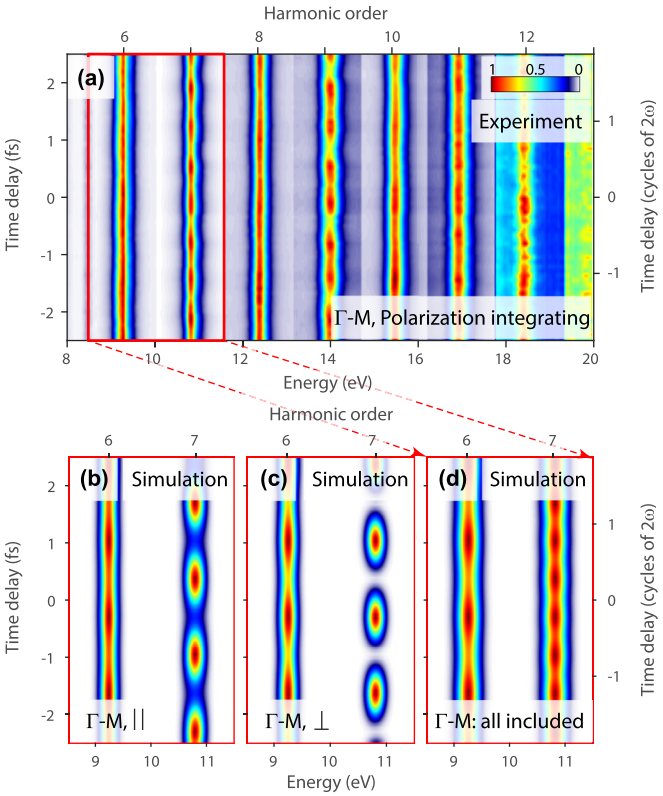

FIG. 4. Two-color interferometry with a polarization-integrating spectrometer. (a) Measured HHG spectra of α-quartz as a function of the delay between the fundamental and second-harmonic pulse, using a polarization-integrating EUV spectrometer. The crystal is oriented such that the laser polarization is parallel to the Γ-M direction. The red box marks the area that will be reproduced by the semiclassical transport theory (b)–(d). (b), (c) Simulated HHG spectra of α-quartz as a function of the delay between the fundamental and second-harmonic pulses, for parallel and perpendicular polarizations, respectively. (d) Incoherent superposition of the two-color interferograms generated in (b) and (c).

the contrast of our polarizer. It may be used as an indirect measurement of the Berry curvature in the real solids [35].

In the next step, we return to polarization-integrating measurements which are conventionally carried out. When the laser polarization is aligned along the Γ-K direction, the harmonics show two beatings per fundamental period (Fig. SM2 [37]). Interestingly, for the Γ-M direction, a polarization-integrating measurement [Fig. 4(d)] will measure an incoherent sum of the two polarizations [Figs. 4(b) and 4(c)]. As a consequence, depending on the relative phase between the two polarizations of the high-order harmonic emission, the polarization-integrating interferogram shows four beatings per fundamental period, similar to our experimental results shown in Fig. 4(a). Thus this can be a source of confusion where four beatings per fundamental period are usually associated with inversion-symmetric media, which is not the case for α-quartz.

In conclusion, we have shown that two-color interferometry of HHG in solids distinguishes the origin of the broken symmetry, i.e., the lack of inversion symmetry of the solid as opposed to the driving field itself. We showed that polycrystalline SiO_2 macroscopically behaves as an inversion-symmetric solid, similar to fused silica. In contrast, for α-quartz, all odd and even harmonics beat two times per fundamental period in our polarization-resolved interferograms. All of the measured results can be intuitively explained. Broken inversion symmetry of the medium competes with the broken inversion symmetry of the incident electric field, leading to a change of beating patterns, from four to two beatings per fundamental period. The agreement between the experimental results and our numerical simulations furthermore lends support to the intraband excitations as the main mechanism producing HHG from SiO_2, although recent works [48,49] have showed that the distinction of the inter- or intraband currents can depend on the gauge employed. In α-quartz, careful investigation of polarization should be needed to avoid the measurement of polarization-mixed spectra and a potentially misleading interpretation. In inversion-symmetric media such as magnesium oxide, all emitted harmonics have the same polarization as the linearly polarized driving electric fields. Therefore one would not have to use a polarization-resolving spectrometer for the investigation of HHG from inversion-symmetric media. Two-color interferometry in combination with high-order harmonic spectroscopy in solids thus could enable alternative measurements of more complex symmetries, indirect measurement of the Berry curvature, possibly assisting measurements of carrier scatterings in solids, and characterization of the permanent dipole moment of the studied material.

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