Spectral narrowing of phonon signature in time-domain sum-frequency spectroscopy

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Sum-frequency generation (SFG) spectroscopy provides a versatile method for the investigation of non-centrosymmetric media and interfaces. Here, using tunable picosecond infrared (IR) pulses from a free-electron laser, the nonlinear optical response of 4H-SiC, a common polytype of silicon carbide, has been probed in the frequency- and time-domain by vibrational SFG spectroscopy. In the steady-state spectra, resonances originating from IR-active phonons of the bulk crystal are present. Linear optical effects are shown to have a significant contribution to the SFG spectrum. In the time domain, the development of the SFG intensity is linked to the free-induction decay of the induced coherent IR polarization. Close to a vibrational resonance, a slower polarization dephasing is observed compared to off-resonant IR excitation. Thus, temporal separation of IR and up-conversion pulse allows for an enhanced spectral resolution of the phonon modes, as corroborated by model calculations.

I. INTRODUCTION

Lattice vibrations, as an elementary excitation of condensed matter, play a fundamental role for the properties of solids. Thus, investigations of vibrational modes allow for insights into the dynamical behavior of atomic or molecular systems at the microscopic scale [1–3]. In this regard, infrared-visible (IR-VIS) sum-frequency generation (SFG) spectroscopy has proven to be a valuable all-optical method [4]. Besides information about the energy and spectral lineshape of the vibrational excitations, the nonlinear optical character of the technique gives also access to symmetry properties of the investigated system [5, 6]. Thus, interfacial- and surface-specific spectra of vibrational modes, e.g. of adsorbed species, can be studied [7, 8]. In addition, time-resolved SFG spectroscopies directly elucidate the energy and phase relaxation dynamics of the vibrational states [9, 10].

Whereas IR pump-SFG probe spectroscopy is utilized to measure the lifetime $T_1$ of a vibrational population, the dephasing time $T_2$ of the induced polarization can be directly obtained from time-domain SFG spectroscopy [11]. There, the IR pulse excites a coherent polarization whose decay is subsequently probed by the time-delayed VIS pulse. The measured phase relaxation, also called free-induction decay (FID), is linked to the SFG spectrum via Fourier transform [12]. Thus, deviations in the FID affect the spectral response and vice versa. Previous IR-VIS SFG studies have investigated the effect of linear and nonlinear optical properties on the static spectra of solid materials [13, 14] as well as both the frequency- and time-domain response of adsorbate vibrations [9] and interfacial systems [15, 16].

Here, the SFG response of bulk phonons in silicon carbide, a robust semiconducting crystal with a broad range of applications [17], has been investigated. Besides an examination of the vibrational modes in the steady state, time-domain SFG measurements are performed on a femtosecond timescale. Thus, the experimental data allow to analyze the relation between the free-induction decay and changes in the transient SFG spectra. Further, model simulations of the time-domain SFG response are compared with the observed behavior. Finally, consequences for the spectral resolution in time-resolved SFG experiments are discussed.

II. EXPERIMENTAL SYSTEM

The spectral and time-domain nonlinear optical response of the vibrational modes is investigated by IR-VIS SFG spectroscopy. This technique employs an IR pulse with frequency $\omega_1$ for resonant excitation of the vibrational mode, while the following pulse in the VIS spectral range (frequency $\omega_2$) leads to the emission of a photon at the sum frequency $\omega_3 = \omega_1 + \omega_2$. By scanning the IR stimulus $\omega_1$ during constant up-conversion frequency $\omega_2$, the detected SFG intensity $I(\omega_3)$ reveals the vibrational spectrum of the investigated system. In contrast, recording $I(\tau)$ by tuning the time delay $\tau$ between both pulses at fixed wavelengths gives direct access to the time-domain dynamics of the induced IR polarization [12].

The coherent IR radiation with a continuously tunable center wavelength between 3 µm and 50 µm has been obtained from a free-electron laser (FEL) oscillator [18]. There, the repetition rate of the accelerated electron bunches is imprinted on the temporal structure of the IR emission, delivering ps-short FEL micro-pulses at a rate of 55.5 MHz within a $\sim 10$ µs-long macro-pulse. The duration, and thus bandwidth, of the micro-pulses can be adjusted via shortening of the FEL cavity length $L$, described as the cavity detuning $\Delta L$ [19].

The VIS up-conversion radiation is derived from a table-top NIR fiber oscillator, providing bandwidth-limited 100 fs-short pulses at 1055 nm wavelength and 55.5 MHz repetition rate. Half of the NIR power is frequency-doubled in a 1 mm thick, type I phase-
matched BBO crystal, whereas the remaining light is used for a balanced optical cross-correlator (see below). For the measurement of the static SFG spectra, the VIS pulses are stretched in a strongly dispersive SF11 glass to about 1 ps duration (FWHM), increasing the temporal overlap with the IR FEL pulses. In the time-domain experiments, the original 120 fs VIS pulses pass a delay stage before being focused onto the sample. The temporal overlap of IR and VIS pulses is accomplished by an RF synchronization system between the FEL master oscillator and the table-top laser, see Ref. [19] for details.

Static SFG spectra are acquired within a reflection geometry. There, the angle of incidence (AOI) of the IR radiation is 55°, whereas the VIS light is incident under 30°. Due to momentum conservation, the generated sum-frequency radiation is emitted close to the propagation direction of the reflected VIS beam. Spectral and polarization filtering is used before SFG intensity detection by a photomultiplier tube. The linear polarization of IR and VIS radiation can be adjusted via half-wave plates. In the time-domain spectroscopy measurements, the sample is mounted with its surface normal parallel to the VIS wavevector and the transmitted SFG radiation is detected. In parallel, a balanced optical cross-correlator (BOC) [20] monitors the actual FEL – table-top laser pulse timing. For that, a part of the NIR radiation is mixed with 15 % of the FEL power generated SFG intensity is strongly determined by the point group symmetry 6

The investigated sample is a 350 µm thin, c-cut semi-insulating silicon carbide crystal of polytype 4H. Due to the point group symmetry 6mm [21], the hexagonal crystal exhibits birefringent linear optical properties. Further, the lack of an inversion center allows for a nonzero electric dipole contribution to a second-order nonlinear optical susceptibility \( \chi^{(2)} \) [22, 23]. The wide band gap of \( E_g = 3.2 \text{ eV} \) [17] inhibits electronic excitations by visible photons, while the strong Si-C bonds within the large crystal unit cell give rise to multiple vibrational modes in the mid-infrared spectral region [21], causing the so-called Reststrahlen band [24]. Spectroscopic measurements have been performed at ambient conditions.

III. STATIC SUM-FREQUENCY SPECTRUM

A. Theoretical Model

For polar dielectric materials, the sum-frequency response is dominated by the electric-dipole contribution from the bulk phase. Thus, the spectral behavior of the generated SFG intensity is strongly determined by the dispersion of both the linear and second-order nonlinear optical susceptibilities. Within the established theoretical model, the SFG signal is given by [6, 14]

\[
I(\omega_3) \propto \left| \mathbf{F}(\omega_3) \cdot \mathbf{F}(\omega_1) \cdot \mathbf{F}(\omega_2) \right|^2 \cdot \frac{1}{\Delta k^2},
\]

(1)

with the Fresnel factor \( \mathbf{F}(\omega) \), the bulk susceptibility \( \chi^{(2)}_B \) and the wavevector-mismatch \( \Delta k \). In the case of optical anisotropic media, the dielectric function \( \epsilon(\omega) \) as well as the second-order susceptibility \( \chi^{(2)}_B \) obtain tensorial character, where symmetry properties of the crystal structure limit the number of independent non-vanishing components. The polarizations of the incident and emitted electric fields \( \mathbf{E}(\omega_i) \) are accounted for in the nonlinear response function, Eq. (1), by the unit vectors \( \hat{e}_p(\omega_i) = (\cos \theta_i, 0, \sin \theta_i) \) or \( \hat{e}_s(\omega_i) = (0, 1, 0) \) for p- or s-polarized waves, respectively. The angle of incidence or emission of field \( \mathbf{E}(\omega_i) \) relative to the surface normal is denoted by \( \theta_i \).

The Fresnel factors describe the behavior of an optical field transversing the interface of two different media. For the case of an isotropic medium (labeled I) next to an uniaxial crystal (II) whose surface normal is parallel to the optic axis along z-direction (c \( \parallel \) z), the Fresnel coefficients are [24, 25]

\[
\begin{align*}
F_{xx} &= \frac{2g^I g^I}{g^I + g^I}, \\
F_{yy} &= \frac{2g^I}{g^I + g^I}, \\
F_{zz} &= \frac{\epsilon^{II}}{\epsilon^{II}} \frac{2g^I}{g^I + g^I}.
\end{align*}
\]

(2)

The dispersion functions of the anisotropic medium are part of the dielectric tensor with \( \epsilon_{xx}(\omega) = \epsilon_{yy}(\omega) = \epsilon_{\parallel}(\omega) \) and \( \epsilon_{zz}(\omega) = \epsilon_{\perp}(\omega) \). The relevant z-components of the wavevector \( g \equiv k_z \) read

\[
\begin{align*}
g^I(\omega, \theta) &= \frac{\omega}{c_0} \sqrt{\epsilon^I(\omega) \cos \theta}, \\
g^I_{\parallel}(\omega, \theta) &= \frac{\omega}{c_0} \sqrt{\epsilon^I_{\parallel}(\omega) - \sin^2 \theta}, \\
g^I_{\perp}(\omega, \theta) &= \frac{\omega}{c_0} \sqrt{\epsilon^I_{\perp}(\omega)} \sqrt{\epsilon^I(\omega) - \sin^2 \theta},
\end{align*}
\]

(3)

with the angle of incidence \( \theta \) relative to the surface normal. The birefringence of the uniaxial crystal is taken into account by distinguishing the propagation of ordinary and extraordinary beam, denoted as o and e, respectively.

The phonon resonances in the linear dielectric function of the crystal are modeled as Lorentz-type oscillators. Within the infrared spectral range, where the
Reststrahlen effect is observed, the following function is used [26],
\[ \varepsilon_p(\omega_1) = \varepsilon_{p,\infty} \left( 1 + \sum_r \frac{\omega_1^2 - \omega^2_{TO,r,p} - i\gamma_{TO,r,p}}{\omega^2_{TO,r,p} - \omega_1^2 - i\gamma_{TO,r,p}} \right) \]
with the high-frequency dielectric constant \( \varepsilon_{p,\infty} \), the frequencies \( \omega_{TO,r,p} \) and dampings \( \gamma_{TO,r,p} \) of the IR-active TO phonon resonances \( r \). The numerator \( \omega_1^2 - \omega^2_{TO,r,p} \) represents the oscillator strength. Each quantity is given in the basal plane (\( p = \perp \)) and parallel to the \( c \) axis (\( p = || \)) of the anisotropic crystal, respectively.

In the same way, the dispersion of the second-order susceptibility tensor components \( \chi^{(2)}_{ijk}(\omega_3,\omega_2,\omega_1) \) is modeled as sum of a constant contribution and an IR-frequency dependent Lorentz oscillator for each SFG-active phonon frequencies \( \nu \). The number of independent components of the \( \chi^{(2)}_{ijk} \) tensor is governed by the point group symmetry of the crystal [28]. Usage of the second-order tensor in accordance with the experimental arrangement requires a transformation from the crystallographic framework \( (i,j,k) \) \( \in \{a,b,c\} \) with the principal axes \( a,b,c \) and \( c \) to the laboratory coordinates \( (l,m,n) \) \( \in \{x,y,z\} \) as given by
\[ \chi^{(2)}_{lmn} = \sum_{ijk} \chi^{(2)}_{ijk}(\hat{e}_l \cdot \hat{e}_i)(\hat{e}_m \cdot \hat{e}_j)(\hat{e}_n \cdot \hat{e}_k). \]

The wavevector mismatch \( \Delta k = |\vec{k}(\omega_3) - \vec{k}(\omega_2) - \vec{k}(\omega_1)| \) inside the investigated material extends along the \( z \)-direction \( \Delta k = \Delta k_z = \Delta q \) since the momentum parallel to the interface is conserved. In general, the wavevector \( \vec{k}(\omega_i) \), Eq. (3), is a complex quantity, reducing to \( |\vec{k}(\omega_i)| = \omega_i / \varepsilon_0 \) with refractive index \( n \) only for non-absorbing media.

**B. Experimental Results and Analysis**

The static sum-frequency generation spectrum of the 4H-SiC crystal is obtained with zero time delay \( (\tau = 0) \) between IR excitation and VIS up-conversion pulse. Using the reflection geometry, SFG spectra under different polarization combinations have been measured, summarized in Fig. 1. Here, the state of polarization of incoming and generated beams is denoted in the order
\[ \nu = \nu_{IR} = 750 \text{ cm}^{-1} \]
\[ 800 \]
\[ 850 \]
\[ 900 \]
\[ 950 \]
\[ 1000 \]
\[ 1050 \]

**FIG. 1.** Experimental SFG spectra of 4H-SiC. The SFG intensity is depicted as function of the IR wavenumber for different polarization conditions around the Reststrahlen band (gray area), limited by the TO and LO phonon frequencies.

\( \tilde{\varepsilon}(\omega_3), \tilde{\varepsilon}(\omega_2), \tilde{\varepsilon}(\omega_1) \). Note that the spectra are plotted as function of the incident IR wavenumber \( \nu_{IR} \).

Strong sum-frequency emission is observed in the cases of PPP and SSP polarization. There, a distinct double-peak structure of the SFG intensity arises around \( \nu_{IR} \sim 960 \text{ cm}^{-1} \). In contrast, no significant SFG signal is measured at all under SPP, PSP and PPS conditions within the investigated spectral region of \( \nu_{IR} = 750 \text{ cm}^{-1} \) to 1050 cm\(^{-1} \).

To rationalize the experimental findings, information about the number and symmetry properties of the vibrational modes are required. The characteristics of relevant optical phonons are summarized in Tab. I. Within the basal plane, the vibrational modes \( \omega_{TO/LO,\perp} \) at the \( \Gamma \) point obey \( E_1 \) symmetry, whereas the lattice oscillations \( \omega_{TO/LO,||} \) polarized in the direction of the optic axis are \( A_1 \) symmetric [26]. The \( A_1 \) and \( E_1 \) phonons are all Raman active [21]. However, only the transverse vibrations can be excited by IR absorption [29].

At first sight, the measured spectral features might seem unreasonable, since at the position of the TO phonon, which is IR as well as Raman active and thus SFG-allowed [6], no peak is observed. On the other hand, the SFG intensity increase around the LO vibration can not be caused by a resonant enhancement of the second-order susceptibility due to the dipole-forbidden IR transition.

A fit of the spectra with the sum-frequency model developed in Eq. (1) enables a disentanglement of the different factors contributing to the SFG signal. Due to point group \( 6mm \) of the 4H-SiC crystal bulk [21], the
TABLE I. Optical phonon frequencies of 4H-SiC at the Brillouin zone center in the Reststrahlen band. The values of phonon energy $\nu$ and damping $\gamma$ are extracted from a fit of the SFG spectra using Eq. (1). Symmetry properties and IR / Raman activities are taken from Ref. [21]. Planar modes ($\perp$) are IR active in the ordinary ray, axial modes ($||$) are excited with the extraordinary ray.

| Mode Symm. $\nu$ (cm$^{-1}$) $\gamma$ (cm$^{-1}$) IR-active Raman-active |
|-----------------|-----------------|---------------|
| $TO_1$          | $A_1$           | 787.2         | x  | x  |
| $LO_1$          | $A_1$           | 962.3         |   | x  |
| $TO_\perp$      | $E_1$           | 797.6         |  5.0 | x  |
| $LO_\perp$      | $E_1$           | 968.5         |   | x  |

Second-order susceptibility tensor $\chi^{(2)}_{ij}$ has the following four independent, non-vanishing components, given in Cartesian coordinates [28]:

$$\chi^{(2)}_{zzz}, \chi^{(2)}_{zzx}, \chi^{(2)}_{zyy}, \chi^{(2)}_{yy} = \chi^{(2)}_{xyz}, \chi^{(2)}_{yz}.$$

(7)

Within the investigated spectral range, the only resonant contribution to linear (Eq. (4)) and second-order (Eq. (5)) optical susceptibilities arises due to a TO phonon mode, thus a single Lorentz term is sufficient for the description of the dispersion relation. The relevant vibrational modes $\omega_{LO/TO,p}$ have to be considered in the model when the IR field polarization $E(\omega_{1})$ is either parallel ($p = ||$) or perpendicular ($p = \perp$) to the z-axis.

Free fitting parameters are the phonon frequencies $\omega_{LO/TO,p}$ and dampings $\gamma_{TO,p}$, entering both into the dielectric function $\varepsilon_p(\omega)$ and the second-order susceptibility $\chi_{ijk}(\omega)$, as well as the non-resonant constants $\chi^{(2)}_{i\neq j\neq k\infty}$ and resonance amplitudes $A_{r,ijk}$ of the nonlinear susceptibility. The obtained phonon values are listed in Tab. I. Parameters of the dielectric function used in the IR region, Eq. (4), are taken from Ref. [26], whereas Sellmeier equations, $\varepsilon_\perp(\omega) = n^2_\perp(\lambda)$ and $\varepsilon_{||}(\omega) = n^2_{||}(\lambda)$, are employed in the VIS range [30].

The different contributions to the SFG spectrum in the case of PPP polarization, as extracted from the fit result, are displayed in Fig. 2. Experimental data and fitted curve show reasonable agreement, see Fig. 2(a). The nonlinear origin of the emitted radiation, captured by the dispersive $\chi^{(2)}$ tensor, is plotted with its absolute components $|\chi^{(2)}_{ijk}|^2$ in Fig. 2(b). Since the spectral variation of the up-converted radiation $\omega_3$ is rather small, only the IR frequency dependence of the second-order susceptibility $\chi^{(2)}(\omega_3)$ is taken into account. In the case of PPP polarization, all independent tensor components contribute to the SFG signal. A resonant enhancement of the nonlinear susceptibility $\chi^{(2)}(\omega_3)$ of about two orders of magnitude is observed around the SFG-active TO phonon. Depending on the relevant tensor component, the peak occurs either at the axial ($\omega_{TO,||}$) or planar ($\omega_{TO,\perp}$) TO mode.

FIG. 2. Sum-frequency generation in the Reststrahlen region of 4H-SiC. Shown are (a) the total intensity as measured and fitted with the model of Eq. (1), (b) the IR dispersion of the quadratic susceptibility tensor components, (c) the Fresnel factors $|F_{ll}|^2$ governing the transmission of the IR field at the air/SiC interface and (d) the phase mismatch between IR, VIS and SFG waves inside the nonlinear crystal. Depending on the propagation direction of the SFG radiation (forward, backward), the mismatch and hence the amplitude and spectral behavior of the emitted SFG light are affected. The broad range of the Reststrahlen band is indicated (gray area). Data are for PPP configuration.
To explain the difference of the peak positions in the measured SFG spectrum and the second-order susceptibility, linear optical effects have to be invoked [14]. On the one hand, the Fresnel factors, Eq. (2), depicted as $|F_{ij}(\omega_1, \theta_1)|^2$ in Fig. 2(c), modify the actual field strength within the material. For a $p$-polarized field $E(\omega)$, only the factors $F_{xx}$ and $F_{zz}$ are relevant. Reduced IR transmission at the crystal-air interface occurs for $\omega_1$ close to $\omega_{TO}$ due to the strong vibrational absorption of the crystal. Within the Reststrahlen band, the dielectric function is characterized by a negative real part. At the other boundary of the band, towards the LO vibration $\omega_{LO}$, the Fresnel factor is increased due to a near-zero permittivity. In particular, the out-of-plane component $F_{zz}E_z$ of the electric field rises by three orders of magnitude. Due to the optical anisotropy of the 4H-SiC crystal, both $\omega_{LO//}$ and $\omega_{LO\perp}$ enter as singularities into $F_{zz}$, Eq. (2), causing two spectrally separated peaks of the electric field enhancement. This effect is absent in the case of normal incidence ($\theta_1 = 0$), also shown in Fig. 2(c), where the crystal essentially shows an isotropic response.

On the other hand, the dielectric dispersion affects the wavevector mismatch $\Delta k(\omega_1)$ inside the nonlinear medium. Depending on the observation of the SFG radiation either transmitted or reflected from the crystal, the propagation of the sum-frequency wavevector radiation either transmitted or reflected from the crystal, medium. Depending on the observation of the SFG response.

Consequently, the linear optical effects of Fresnel transmission and wavevector mismatch strongly modify the SFG spectrum. The contribution of the resonant enhancement of $\chi^{(2)}(\omega_1)$ at the TO phonon frequency $\omega_{TO}$, is suppressed by the reduced electric field strength $F_{zz}(\omega_1)|E(\omega_1)|$ and increased phase-mismatch $\Delta k(\omega_1)$. Instead, a (double) peak of the SFG intensity is induced at the LO mode $\omega_{LO}$, mainly caused by the enhanced Fresnel transmission of the out-of-plane component of the electric field $F_{zz}E_z$. A similar behavior is observed for the SFG spectra at other polarization conditions with non-vanishing $\chi^{(2)}$ components (Fig. 1).

The coherence length $l_c$, describing the extent of the bulk volume contributing to the SFG signal, is related to the phase-mismatch via $l_c(\omega) \sim 1/\Delta k(\omega)$ [27]. For the PPP case, the calculated IR frequency dependence $l_c(\omega_1)$ is shown in Fig. 3. In the forward direction, the interaction depth amounts to about one VIS wavelength, $l_c \sim \lambda_2$, whereas the backward SFG emission is limited to a smaller, mainly wavelength-independent region of $l_c \sim 15 \text{nm}$. In relation to the lattice constant $c$ (along the $z$ direction), the latter case corresponds to a size of about 15 crystal unit cell. For nonlinear material being opaque to the IR or VIS radiation, absorption would reduce the coherence length even further [27]. Thus, in reflection-type measurements of non-centrosymmetric materials, the coherent SFG process is sensitive to just a thin volume beneath the surface – typically tens of nanometers [31] – although the bulk response is being probed.

Regarding the value of the susceptibility components $\chi^{(2)}_{ijkl}$, only the ratio of the tensor elements can be extracted. The $|\chi^{(2)}_{zzz}|$ is stronger than the other non-vanishing components, cf. Fig. 2(b). In comparison to reported experimental values for the quadratic nonlinear optical coefficients of 4H-SiC in the IR region, $\chi^{(2)}_{zzz}/\chi^{(2)}_{xxx} = -4.5 \text{ pm/V}$ [22] and $|\chi^{(2)}_{zzz}| \approx |\chi^{(2)}_{xxx}| \approx 6.5 \text{ pm/V}$ [23], the SFG measurement is in reasonable agreement. Calculated second-order susceptibilities, based on density functional theory, support the experimental results [32, 33]. Moreover, it has been found that the optical nonlinearity is increased for SiC polytypes of reduced hexagonality (e.g. 6H, 3C), which possess also a smaller band gap [22].
IV. TIME-DOMAIN SUM-FREQUENCY DYNAMICS

A. Model

In time-domain SFG measurements, the control of the temporal delay $\tau$ of the IR excitation pulse $E_{IR}$ versus the VIS up-conversion field $E_{VIS}$ provides insights into the dephasing dynamics of the induced coherent IR polarization $P^{(1)}(t)$ [11]. Thus, by recording the spectrally integrated SFG intensity as a function of the delay, $I_{SFG}(\tau)$, the free-induction decay (FID) of the linear polarization $P^{(1)}(t)$ can be captured [9].

An analytical model of the time-domain SFG process allows to calculate the signal intensity $I_{SFG}(\tau)$. Starting from the IR pulse $E_{IR}(t)$, the interaction with the investigated system, characterized by a response function $R(t)$, causes a first-order polarization $P^{(1)}(t)$ [6, 16]:

$$P^{(1)}(t) = \int dt' E_{IR}(t - t') R(t'). \quad (8)$$

In case of resonant excitation of the system, a long-lasting coherent polarization is induced, dephasing over time. In the meantime, the arriving up-conversion pulse $E_{VIS}(t - \tau)$ creates the nonlinear polarization $P^{(2)}(t)$,

$$P^{(2)}(t, \tau) \approx E_{VIS}(t - \tau) P^{(1)}(t). \quad (9)$$

Due to the non-resonant field $E_{VIS}$, an instantaneous interaction with the linear polarization $P^{(1)}(t)$ has been assumed, thus not requiring a convolution integral. Finally, the SFG intensity emitted by the second-order polarization,

$$I_{SFG}(\tau) \propto \int dt |P^{(2)}(t, \tau)|^2, \quad (10)$$

is received in dependence on the time delay $\tau$.

B. Free-Induction Decay of IR Polarization

The dephasing of the induced dielectric polarization $P^{(1)}(t)$ in 4H-SiC has been studied close to the LO phonon mode. Although the vibration at $\nu_{LO}$ is not an SFG-active $\chi^{(2)}$ resonance, the phonon-related modulation of the linear optical response $R = F(\nu)$ provides for a strong SFG signal, as discussed previously in Sec. III B. All time-domain measurements have been performed in PPP polarization configuration. For the IR excitation, the length of the FEL pulse has been chosen as short as possible by using a small cavity detuning $\Delta L = 1\lambda$. The SFG transients $I_{SFG}(\tau)$ obtained at different excitation frequencies $\nu_{IR}$ around $\nu_{LO} \approx 960 \text{ cm}^{-1}$ are plotted in Figs. 4(a),(b), after BOC correction of the delay values $\tau$.

Clear differences in the behavior of the IR polarization $P^{(1)}(t)$ can be derived from the SFG graphs $I_{SFG}(\tau)$, Fig. 4(a): The spectral dependence of the peak amplitude is explained in terms of the Fresnel factor $F(\nu)$, i.e. linear optical effects. With regard to the dynamics, a slower free-induction decay $P^{(1)}(t)$ is observed for the excitation at $\nu_{IR} = 1000 \text{ cm}^{-1}$ compared to the off-resonant trace at $\nu_{IR} = 900 \text{ cm}^{-1}$. This is obvious from the semilogarithmic plots in Fig. 4(b). Further, a small temporal shift of the peak position by about 400 fs towards positive delay times is detected in the resonant case, cf. Fig. 4(a).

In order to compare the dephasing dynamics at the different excitation frequencies $\nu_{IR}$, decay constants are extracted from the experimental data. To this end, a fit of the measured transients is performed with the convolution of a reference FEL pulse shape and a step-like exponential function of the form

$$f(\tau) = H(\tau) e^{-\tau/\kappa}, \quad (11)$$

where $H(\tau)$ is the Heaviside distribution. The resulting SFG intensity decay times $\kappa$ are displayed in Fig. 4(c).
The IR excitation in the vicinity of the LO phonon mode reveals a larger decay constant of $\kappa = 1.66 \pm 0.01$ ps, compared to the spectrally offset case at $\nu_{IR} = 900 \text{ cm}^{-1}$ with $\kappa = 0.15 \pm 0.01$ ps. Since the SFG intensity is related to the linear polarization via $I \propto |P^{(2)}|^2$ and $P^{(2)} \propto P^{(1)}$, the dephasing time $T_2$ of the IR polarization amounts to $T_2 = 2\kappa$ [12]. Thus, the measured free-induction decay time in bulk 4H-SiC varies between $T_2 = 3.32 \pm 0.02$ ps (LO phonon resonant) and $T_2 = 0.30 \pm 0.02$ ps (off-resonant). Although the LO vibration itself does not absorb the IR light, the presence of the vibrational mode affects the dephasing of the IR polarization.

For comparison, dephasing times of the same order of magnitude have been found in solids for the LO phonon ($T_2 = 4.2 \pm 0.4$ ps [34]) and TO phonon ($T_2 = 2.9 \pm 0.3$ ps [35]) in a semiconducting polar GaAs crystal or the TO mode ($T_2 = 5.8 \pm 0.6$ ps [36]) in insulating diamond at room temperature.

The dynamic dephasing times of the IR polarization has also been visualized using the full FEL pulse profile, see Fig. 5. As reported recently, Ref. [19], the infrared emission of an FEL oscillator can exhibit a sub-pulse structure under certain conditions. There, multiple intensity peaks are present during the ps-short FEL micro-pulse, which give rise to a regular oscillation pattern over the course of the $\mu$s-long IR macro-pulse (see Fig. 5 in Ref. [19]). The incorporation of the sub-pulse dynamics of the FEL into the measured dephasing response of the solid material is depicted in Figs. 5(a)-(c). Here, the BOC-corrected SFG intensity $I_{SFG}(\tau)$ is plotted as function of the time $t$ within an FEL macro-pulse for different IR excitation wavenumbers $\nu_{IR}$.

In Fig. 5(a), the temporal structure of the SFG emission closely follows the original FEL sub-pulse pattern, due to the fast dephasing in the non-resonant case at $\nu_{IR} = 900 \text{ cm}^{-1}$. At the beginning of the macro-pulse, at about $t = 2\mu$s, the first sub-pulse emerges. In the course of time $t$, the peak position is shifted towards a negative delay $\tau$. Meanwhile, the second sub-pulse arises at $t \approx 4\mu$s, undergoing the same delay shift. The commencing of a third sub-pulse is observed near the end of the macro-pulse at $t = 10\mu$s. These observations of the sub-pulse behavior could be well reproduced by FEL simulations based on classical electrodynamics [19, 37].

The variation of the dephasing dynamics with the excitation frequency is apparent in Figs. 5(b) and (c), when looking at the SFG intensity contrast in the temporal range between the sub-pulse peaks. In the resonant case at $\nu_{IR} = 960 \text{ cm}^{-1}$, Fig. 5(c), a clear ‘smear-out’ of the intensity is observed, caused by the relative long decay time $\kappa$, compared to the behavior in Fig. 5(b). The one-dimensional dephasing traces shown in Fig. 4 have been extracted from the plots of Fig. 5 at time $t = 3.5\mu$s, to facilitate the fitting of the material response induced by just a single FEL sub-pulse.

C. Transient SFG Spectra

A further characterization of the polarization dephasing has been carried out in the frequency domain, revealing the SFG spectra $I_{SFG}(\nu_{IR})$ at different delay times $\tau$, see Fig. 6. Here, the spectral response is acquired by scanning the wavenumber $\nu_{IR}$ of the narrow-band FEL radiation (cavity detuning $\Delta L = 4\lambda$) while keeping the delay path relative to the up-conversion pulse constant.

For all measured delay values in Fig. 6, a single resonance peak around $\nu_{IR} = 960 \text{ cm}^{-1}$ is present. This is in contrast to the static SFG spectrum measured in reflection geometry, Fig. 2(a), where two peaks have been observed. The reason is the smaller angle of incidence of
The linewidth extracted from the spectrum at $\tau = 0$ amounts to $21.8 \pm 0.7 \text{ cm}^{-1}$ (FWHM). Compared to the time-domain data ($T_2 = 3.32 \text{ ps}$), a smaller vibrational linewidth $2\Gamma = 1/\pi\sigma_0 T_2 = 3.2 \text{ cm}^{-1}$ would be expected for a homogeneously broadened Lorentzian lineshape [38]. Actually, the observed resonance has an asymmetric, non-Lorentzian profile, cf. Fig. 6. As discussed previously, the peak in the SFG spectra around $\nu_{IR} \approx 960 \text{ cm}^{-1}$ does not originate from a resonant enhancement of the second-order susceptibility $\chi^{(2)}(\nu_{IR})$, which would result in a Lorentzian, but is due to a frequency-dependent modulation of the nonlinear response by the Fresnel factor $F(\nu_{IR})$. In consequence, the free-induction decay traces in the time-domain deviate from an ideal exponential function, cf. Fig. 4. Nevertheless, the fitting result provides a comparative figure.

The development of the normalized spectral lineshape $I_{\text{SFG}}(v_{IR})$ as a function of the temporal delay $\tau$ in Fig. 6 exhibits two main characteristics: First, the wavenumber of the peak position at $\nu \approx 960 \text{ cm}^{-1}$, related to the LO phonon $\nu_{LO}$, remains constant over time. Second, a narrowing of the spectral linewidth $\Delta\nu$ is observed at a larger time delay $\tau$ between the IR excitation and VIS up-conversion pulse. This is accompanied by a transition of the lineshape from the asymmetric to a symmetric form. The extracted peak wavenumbers $\nu$ and bandwidths $\Delta\nu$ (FWHM) of the resonance are summarized in Tab. II. These spectral observations are in line with the frequency-dependent dephasing measurements in the time-domain, cf. Fig. 4. The faster off-resonant decay of the induced IR polarization entails a spectral narrowing of the linewidth towards longer delay values.

### Table II. Development of peak frequency $\hat{\nu}$ and bandwidth $\Delta\nu$ of the SFG resonance as function of the IR-VIS pulse delay $\tau$. The values are extracted from the transient spectra shown in Fig. 6.

| Delay $\tau$ (ps) | 0 | 3 | 6 |
|------------------|---|---|---|
| Peak $\hat{\nu}$ (cm$^{-1}$) | 959.3 ± 0.2 | 959.3 ± 0.1 | 958.9 ± 0.1 |
| FWHM $\Delta\nu$ (cm$^{-1}$) | 21.8 ± 0.7 | 18.1 ± 0.5 | 13.1 ± 0.3 |

### D. Simulation

To support the experimental results, simulations of the transient SFG response have been performed. Following the theoretical model in Sec. IV A, the temporal dephasing of the material’s first-order polarization $P^{(1)}(t)$, induced by the IR excitation, is studied. The response function $R(\nu)$ of the SiC crystal in the frequency domain is characterized by the Fresnel factor $F(\theta, \nu)$, considering the resonance near the LO phonon mode. Taking into account a Gaussian pulse shape, the IR pulse can be described by a variable center wavenumber $\nu_0$ and a fixed spectral width $\sigma_\nu = 0.441/2\sqrt{2\ln 2}\nu_\text{IR}$ related to the pulse duration $\tau_\text{IR}$,

$$E_{\text{IR}}(\nu) = \hat{E}\nu^{-\nu_0^2/2\sigma_\nu^2}.$$  \hspace{1cm} (12)

The resulting linear polarization, given by

$$P^{(1)}(\nu) \propto |F(\nu)E_{\text{IR}}(\nu)|,$$ \hspace{1cm} (13)

is subsequently Fourier-transformed to obtain the free-induction decay in the time-domain,

$$P^{(1)}(t) = \mathcal{F}(P^{(1)}(\nu)).$$ \hspace{1cm} (14)

Insertion of the IR polarization $P^{(1)}(t)$ into Eqs. (9) and (10) yields the time-evolution of the SFG intensity, $I_{\text{SFG}}(\tau)$. The spectral dependence $I_{\text{SFG}}(\tau, \nu)$ is calculated by tuning of the IR wavenumber $\nu_0$ in Eq. (12).

The simulation results of the time- and frequency-dependent SFG intensity are depicted in Fig. 7. The chosen calculation conditions are a close to normal incidence of the IR excitation with $\theta_{\text{IR}} = 25^\circ$, a pulse duration of $\tau_\text{IR} = 2 \text{ ps}$ and a PPP polarization configuration, corresponding to the measurement situation. In Fig. 7(a), the two-dimensional plot shows a single resonance, located around $\nu_{\text{IR}} = 962 \text{ cm}^{-1}$, decaying in intensity on a ps-time scale. The normalized SFG spectra $I_{\text{SFG}}(\nu_{IR})$ at certain time delays $\tau$ are displayed in Fig. 7(b). On the one hand, an asymmetric lineshape is present at zero delay. Towards larger delay times, the resonance profile turns symmetric. On the other hand, a narrowing of the spectral linewidth is observed at increased pulse delays, e.g. to 32% of the original FWHM after $\tau = 4 \text{ ps}$. These theoretical findings are in qualitative agreement with the measured behavior, cf. Fig. 6.
FIG. 7. Simulation of the time-domain SFG response of a single resonance. (a) Two-dimensional plot of the SFG intensity $I_{\text{SFG}}(\tau, \nu_{\text{IR}})$, showing an intensity decay due to polarization dephasing. (b) Transient normalized SFG spectra $I_{\text{SFG}}(\nu_{\text{IR}})$ around the resonance $\nu_0 = 962 \text{ cm}^{-1}$ at certain time delays $\tau$. (c) Free-induction decay of the SFG intensity $I_{\text{SFG}}(\tau)$, depicted for different IR excitation wavenumbers $\nu_{\text{IR}}$. An exponential fit to the trace at $\nu_0 = 962 \text{ cm}^{-1}$ is also shown (gray line).

In Fig. 7(c), the simulated temporal development of the SFG intensity $I_{\text{SFG}}(\tau)$ is depicted for different excitation wavenumbers $\nu_{\text{IR}}$. There, the intensity reflects the free-induction decay of the induced linear polarization $P^{(1)}(t)$. Obviously, an off-resonant IR excitation yields a faster dephasing than in the resonant case. For excitation at the LO phonon wavenumber, $\nu_{\text{IR}} = 962 \text{ cm}^{-1}$, a decay time of $\kappa = 0.7 \text{ ps}$ might be extracted from an exponential fit. However, the calculated SFG trace deviates from the exponential form, see Fig. 7(c). This is in accordance with the non-Lorentzian lineshape in the calculations, Fig. 7(b). Also, the experimental SFG time-domain traces in Fig. 4(b) exhibit a slight deviation from the exponential decay. Consequently, the applied model simulations provide a valuable description of the experimental observations.

V. CONCLUSION

Combined time- and frequency-domain IR-VIS sum-frequency generation spectroscopy has been performed on vibrational resonances in a semi-insulating, non-centrosymmetric crystal of silicon carbide. Whereas only phonon modes of both IR- and Raman-activity are allowed for a resonant enhancement of the second-order susceptibility $\chi^{(2)}$, Fresnel effects are observed to strongly modify the SFG spectra. In the time-domain, a free-induction decay of the SFG intensity on a ps-timescale is detected, caused by the dephasing of the induced coherent IR polarization. At phonon resonances, a slowdown of the dephasing time $T_2$ has been observed. Using a temporal delay between the excitation and up-conversion pulse, a smaller resonance linewidth has been demonstrated. The experimental results are supported by model simulations of the transient SFG response.

Actually, time-domain SFG spectroscopy studies have shown a higher sensitivity to the resonant part in the SFG process if IR and VIS pulses are temporally separated, avoiding the non-resonant, instantaneous contribution of the second-order susceptibility $[15, 39]$. Thus, the lineshape in the frequency domain is only determined by the resonance dephasing, providing a reasonable way to enhance the spectral resolution. However, one should note that spectral distortions might occur due to phase shifts $[40]$. 
FIG. 8. Post-correction of FEL pulse timing. The time-domain SFG intensity trace, $I_{\text{SFG}}(\tau)$, is shown in the upper panel (a) as measured and after application of the delay correction using the (b) kinetic electron energy monitoring (BPM) or the (c) balanced optical cross-correlation (BOC), respectively. Displayed traces are obtained after timing correction on a macro-pulse level and subsequent averaging. The quality of the results is assessed by comparing with the best-fit to the BOC-corrected SFG transient in (c) using Eq. (A.1), depicted as gray line in (a) to (c). Lower panel shows the calculated intensity differences between data and fit.

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Appendix: Timing Correction

The implementation of the balanced optical cross-correlator (BOC) as well as the characterization of the timing jitter and drift at the employed FEL has been reported previously [19]. Here, the BOC is used as timing monitor in parallel with the time-resolved measurement to compensate for drifts by subsequent post-processing of the acquired data. For that, the timing value $\delta \tau$ received from the calibrated BOC is added to the delay setting $\tau$ to obtain the actual timing $\tau + \delta \tau$ for each FEL macro-pulse. Subsequently, the SFG intensity at the original delay point, $I(\tau)$, is retrieved by linear interpolation and averaging over multiple ($\sim 20$) macro-pulses per delay point.

The results of the timing correction applied to the time-domain SFG measurement are shown in Fig. 8. While the raw data are displayed in Fig. 8(a), the BOC-adjusted SFG trace is plotted in Fig. 8(c). To quantify the improvement in the data quality after correction, a model function is fitted to each curve and the root-mean-square-deviation (RMSD) is calculated. The model function, a convolution integral of a Gaussian pulse shape with an exponentially decaying material response, is

$$I(\tau) = I_0 \exp \left( \frac{\sigma^2}{2\kappa^2} - \frac{\tau - \tau_0}{\kappa} \right) \left( 1 - \text{erf} \left( \frac{\sigma^2 - \kappa(\tau - \tau_0)}{\sqrt{2}\sigma\kappa} \right) \right),$$

(A.1)

with the pulse width $\sigma$, decay constant $\kappa$ and delay zero at $\tau_0$. The reduced RMSD of the BOC-corrected data, $6.5 \times 10^{-3}$, compared to the uncorrected measurement, $9.6 \times 10^{-3}$, reveals the improvement in the data quality.

In addition, the electron beam-position monitoring (BPM) of the accelerator-driven FEL has been employed for timing correction, see Fig. 8(b). Due to the correlation between kinetic electron energy and pulse arrival time (cf. Ref. [19]) with a correlation coefficient of $\rho = 0.65$, a RMSD of the BPM-corrected curve of $8.2 \times 10^{-3}$ could be achieved. Thus, a post-processing of the FEL pulse timing merely based on the monitoring of the electron beam characteristics might provide an alternative method, especially if the optical cross-correlation is difficult to obtain (e.g., due to the used FEL wavelength) [41]. However, the correction accuracy is usually lowered compared to the all-optical timing tool.

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