Supporting Information

Plasmonic terahertz nonlinearity in graphene disks

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1. Summary of parameters for numerical calculations

	Symbol	Name	Value
	ϵ_F	Fermi energy	350 meV
	v_F	Fermi velocity	10^8 cm/s
	μ_c	Carrier mobility	3600 $cm^2/V{\cdot}s$
	W	Effective width of disk	1480 nm
	Λ	Disk period	1850 nm
	η	Filling factor = $\pi R^2/\Lambda^2$	0.6
	n	Carrier density	9×10^{12} (cm^{-2})
	$\Gamma_0=\frac{ev_F}{\sqrt{\pi n}\mu_c\hbar}$	Scattering rate (Plasmon line width)	8.7 ps^{-1}
	$D_{p0}=\sqrt{\pi n}e^2v_F/\hbar$	Drude weight	0.13 $\Omega^{-1}ps^{-1}$
	ω_{PO}^*	Plasmon frequency	$2\pi\times3.5$ THz
	$\omega_{PO}(\theta)=\omega_{PO}^*\left(1-\frac{\pi^2k_B^2\theta^2}{12\epsilon_F^2}\right)$	Electronic temperature θ-dependent plasmon frequency	
	θ_L	Lattice temperature	10 K
	$\alpha_s=\frac{2\pi k_B^2\epsilon_F}{3\hbar^2v_F^2}$	Specific heat	2.01×10^{-13} $J/cm^2{\cdot}K^2$
	β_S	Supercollision cooling coefficient	3.7×10^{-5} $W/cm^2{\cdot}K^3$
	ε_2	Dielectric constant of SiC substrate	12.5
	Z_0	Vacuum impedance ($=\sqrt{\mu_0/\varepsilon_0}$)	377 Ω
	Ξ	Pulse duration	20 ps (FWHM)
	R_s	Repetition rate	13 MHz
	Φ	THz beam width	0.7 mm (FWHM)
	γ	LA phonon scattering coefficient	1.264×10^{-3} $K^{-1}ps^{-1}$

Table 1. Summary of parameters for numerical calculation.

In Table 1, we provide specific values of parameters for numerical calculations.

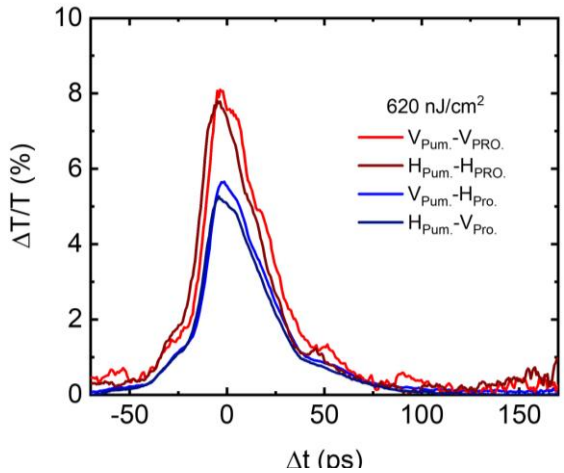

Figure S1. Polarization-dependent pump-probe signal ΔT/T in all four combination to exclude anisotropy effects caused by potentially elliptical disks or cryostat windows. V and H denote the vertical and the horizontal, respectively. Pump and probe are indicated as Pum. and Pro., respectively. All data was measured at the fluence being 620 nJ/cm^2.

2. Polarization-dependent pump-probe signals

3. Optical conductivity calculation for the thermal nonlinearity

The current $\mathbf{j}_\omega^{(1)}$ generated by the linear mechanism has the relation with the electric field $\mathbf{E}$ as $\mathbf{j}_\omega^{(1)}=\sigma_\omega^{(1)}\mathbf{E}$. And, the optical conductivity $\sigma_\omega^{(1)}$ describing the intraband transition in graphene is known to have the Drude-like form:[1,2]

$$\sigma_\omega^{(1)}=\frac{iD_{\mathrm{p0}}}{\pi}\frac{1}{(\omega+i\Gamma_0)} \tag{1}$$

where parameters in Eq. (2) can be referred from Table 1. In order to consider the thermal nonlinearity, we take into account the electronic temperature θ-dependent chemical potential by substituting θ-dependent Drude weight $D(\theta)$ and scattering rate $\Gamma(\theta)$ for D_{P0} and Γ_0 on Eq. (2). $D(\theta)$ and $\Gamma(\theta)$ are:[3]

$$D(\theta)=D_{\mathrm{P0}}\left(1-\frac{\pi^2k_{\mathrm{B}}^2\theta^2}{6\epsilon_{\mathrm{F}}^2}\right),\qquad \Gamma(\theta)=\Gamma_0\left(1+\frac{\pi^2k_{\mathrm{B}}^2\theta^2}{6\epsilon_{\mathrm{F}}^2}\right)+\gamma\theta \tag{2}$$

where k_{B} is Boltzmann constant. Also, to consider the plasmon resonance, equation (2) is tuned by the substitution of $\omega_{\mathrm{eff}}(\theta)=(\omega^2-\omega_{\mathrm{P0}}^2(\theta))/\omega$ onto ω with the filling factor of η.

4. Terahertz (THz) pump pulse

To model the temporal profile of the THz pump beam, a Gaussian shape is employed. Note that pulse duration τ_P is defined by the full width of half maximum (FWHM). Mathematical form of the intensity I(t) of THz pump pulse as a function of the time is given by:

$$I(t)=\frac{Pe^{(-2t^2/(\sqrt{2\ln 2}\cdot\Xi)^2)}}{\left(\frac{\Phi}{2}\right)^2 \pi \cdot R_s \cdot \tau_P} \tag{3}$$

where P is the power.

5. Electronic temperature θ induced by THz pump pulse

The time-dependent evolution of θ induced by the THz pump pulse with center frequency ω_{P0} (3.5 THz) can be obtained by solving the nonlinear thermal equation, as:[4]

$$\alpha_s \theta \frac{d\theta}{dt}+\beta_s\left(\theta^3-\theta_L^3\right)=A(\omega_{P0},\theta)I(t) \tag{4}$$

Here, we assume that the main mechanism of the relaxation is attributed to the supercollision cooling process. $A(\omega_0,\theta)$ is the absorption for the incident THz pump pulse, as:[5]

$$A(\omega_0,\theta)=\frac{4\frac{\sqrt{\varepsilon_1}}{Z_0}\mathrm{Re}[\sigma_{tot}(\omega_{P0},\theta)]}{\left|\frac{\sqrt{\varepsilon_1}}{Z_0}+\frac{\sqrt{\varepsilon_2}}{Z_0}+\sigma_{tot}(\omega_{P0},\theta)\right|^2} \tag{5}$$

where ε_1 and ε_2 are dielectric constants of vacuum and the SiC substrate, respectively.

6. Derivation of pump-induced Kerr-nonlinear conductivity

a) Linear conductivity

First, we consider the linear conductivity, which describes the proportional relationship between the electric field **E** and the current density **J**. In general, the conductivity must be described by a second-rank tensor (3x3 matrix), but in an isotropic optical material, rotational symmetry dictates that the conductivity be proportional to the identity matrix:

$$\boldsymbol{\sigma_{jk}}=\boldsymbol{\sigma^{(1)}}(\boldsymbol{\omega},\theta)\boldsymbol{\delta_{jk}} \tag{6}$$

Hence, the linear conductivity in an isotropic material is described by a single scalar quantity $\boldsymbol{\sigma^{(1)}}(\boldsymbol{\omega},\theta)$, and the linear current points in the same direction as the applied field. We further assume that $\boldsymbol{\sigma^{(1)}}$ depends on the electron temperature θ, which is numerically determined from the heat equation (see above).

b) Nonlinear conductivity

Next, we assume that in addition to the linear conductivity, there is a 3rd-order nonlinear contribution to the conductivity. This could give rise to a variety of nonlinear optical effects, including third harmonic generation, quadratic electrooptic effect, nonlinear refraction, nonlinear absorption, self-focusing, and four-wave mixing. The nonlinear conductivity is described by a 4th rank tensor, σ_{jklm}, with 81 independent complex quantities. However, if we again assume that the material exhibits full rotational symmetry (as would be the case for a fully isotropic material), then this tensor takes the form:

$$\boldsymbol{\sigma_{jklm}}(\boldsymbol{-\omega_4; \omega_1, \omega_2, \omega_3})=\boldsymbol{\sigma_{xyyx}\delta_{jk}\delta_{lm} + \sigma_{xxyy}\delta_{jm}\delta_{kl} + \sigma_{xyxy}\delta_{jl}\delta_{km}} \quad (7)$$

Where for brevity we have suppressed the frequency arguments on the right-hand side terms.

The above equation is completely general, and describes the symmetry properties for all third-order nonlinearities in an isotropic material. Here, we are interested in the case of $\omega_1 = \omega_2 = -\omega_3$, which describes the case of the optical Kerr effect. In this case, Eq. (7) simplifies to:

$$\boldsymbol{\sigma_{jklm}}(\boldsymbol{-\omega; \omega, \omega, -\omega})=\boldsymbol{\sigma_{xyyx}\delta_{jk}\delta_{lm} + \sigma_{xxyy}(\delta_{jm}\delta_{kl} + \delta_{jl}\delta_{km})} \quad (8)$$

where in this case we can use intrinsic permutation symmetry to equate σ_{xyxy}=σ_{xxyy}. So, the optical Kerr effect in an isotropic material can be described in terms of just two quantities. It is convenient to define the dimensionless ratio:

$$\boldsymbol{r} \equiv \frac{\boldsymbol{\sigma_{xyyx}}}{\boldsymbol{\sigma_{xxyy}}} \quad (9)$$

and in the case of bound electron nonlinearities, one often assumes that $\boldsymbol{r} = 1$. With this definition, the nonlinear conductivity can then be written in terms of two quantities $\boldsymbol{r}$ and the diagonal element $\sigma^{(3)} \equiv \sigma_{xxxx}$:

$$\boldsymbol{\sigma_{jklm}}(\boldsymbol{-\omega; \omega, \omega, -\omega})=\boldsymbol{\sigma^{(3)}}\left[\frac{\boldsymbol{r}}{\boldsymbol{1+2r}}\boldsymbol{\delta_{jk}\delta_{lm}} + \frac{\boldsymbol{1}}{\boldsymbol{1+2r}}(\boldsymbol{\delta_{jm}\delta_{kl} + \delta_{jl}\delta_{km}})\right] \quad (10)$$

c) Induced current in pump-probe measurements

We now assume that the electric field is composed of two components (pump = 1 and probe = 2), with complex amplitudes $\mathbf{E}_1$ and $\mathbf{E}_2$, respectively:

$$\mathbf{E}(t)=\frac{\boldsymbol{1}}{\boldsymbol{2}}\mathbf{E_1}\boldsymbol{e^{-i\omega t}} + \frac{\boldsymbol{1}}{\boldsymbol{2}}\mathbf{E_2}\boldsymbol{e^{-i\omega t}} + \boldsymbol{c.c.}, \quad \boldsymbol{|\mathbf{E_1}| \gg |\mathbf{E_2}|} \quad (11)$$

We note that the pump and probe coincide on the sample surface and have the same frequency $\boldsymbol{\omega}$. However, they are ultimately distinguishable from one another in the far field because they have

different **k**-vectors, and that is why we keep track of two separate amplitudes $\mathbf{E}_1$ and $\mathbf{E}_2$.

The induced current will also have two field components associated with the pump and probe:

$$\mathbf{J}(t)=\frac{1}{2}\mathbf{J}_1 e^{-i\omega t}+\frac{1}{2}\mathbf{J}_2 e^{-i\omega t}+c.c.+\cdots \tag{12}$$

where we have omitted the terms corresponding to third-harmonic generation and other nonlinear terms.

Next, the induced probe current amplitude $\mathbf{J}_2$ can be expressed in terms of the pump and probe fields as:

$$J_{2j}=\sigma_{jk}E_{2k}+\frac{3}{2}\sigma_{jklm}E_{2k}E_{1l}E_{1m}^{*}+\frac{3}{4}\sigma_{jklm}E_{1k}E_{1l}E_{2m}^{*} \tag{13}$$

where the first term describes the linear conductivity, and the remaining terms are the non-linear contributions. The "degeneracy" factors of 3/2 and 3/4 appearing in the second and third terms are necessary in order to self-consistently describe the process of cross-modulation of a probe beam by a pump beam. (The degeneracy factor would instead be 1/4 for third-harmonic generation.)

Note that if the pump and the probe were truly co-linear, then the third term (with a degeneracy factor of 3/4) in this expression must be retained in the analysis, and this will give rise to different conclusions about the polarization dependence. However, when there is even a small angle between pump and probe (as in most experiments), phase matching dictates that the final term would produce a third output beam that is spatially separated from the pump, and symmetrically located on the other side with respect to the probe (i.e., located at $2\mathbf{k}_1$-$\mathbf{k}_2$). Here we therefore ignore this term, under the assumption that an aperture in the measurement only records at the angle of the emerging probe beam.

Neglecting the final term, and substituting Eq. (10) into Eq. (13), we arrive at the following expression for the induced sheet current in the probe wave, including both linear and nonlinear contributions:

$$\mathbf{J}_2=\sigma^{(1)}\mathbf{E}_2+\frac{3}{2}\sigma^{(3)}\frac{1}{1+2r}[r(\mathbf{E}_1^{*}\cdot\mathbf{E}_1)\mathbf{E}_2+(\mathbf{E}_1\cdot\mathbf{E}_2)\mathbf{E}_1^{*}+(\mathbf{E}_1^{*}\cdot\mathbf{E}_2)\mathbf{E}_1] \tag{14}$$

When the pump and probe are linearly and co-polarized (say, in the *x* direction), the resulting current **J** will also point in the same direction, allowing us to replace Eq. (14) with a simple scalar equation relating the amplitudes:

$$J_{2x}=\sigma^{(1)}E_{2x}+\frac{3}{2}\sigma^{(3)}|E_{1x}|^2E_{2x} \tag{15}$$

When the pump and probe are linearly polarized and orthogonal to one another, then the final two terms in Eq. (14) vanish, and we find that the resulting current **J** will point in the same direction as the probe. Taking the probe to be *y*-polarized and the pump to be *x*-polarized, we can write:

$$J_{2y}=\sigma^{(1)}E_{2y}+\frac{3}{2}\sigma^{(3)}\frac{r}{1+2r}|E_{1x}|^2E_{2y} \tag{16}$$

If we assume that the pump wave is linearly polarized (say in the *x*-direction), we could superpose the result from Eq. (15) and (16) to obtain a generalized result for the current $\mathbf{J}_2$. However, we note that because the co-polarized and orthogonal cases behave differently, there will in general be a pump-induced change in the polarization state unless one used an *x* or *y* polarized probe. In an experiment, both effects can be separately measured by setting the probe polarization either 45° (or even better, circular polarization) and the inserting a rotatable linear polarizer immediately prior to the detector. We expect to see a fast (pulse-width limited) pump-induced change for both co-polarized and cross-polarized cases, but it will be a stronger in the former.

Next, we assume that the pump and probe are circularly co-polarized. Now the vectors $\mathbf{E}_1$, $\mathbf{E}_2$, and $\mathbf{J}_2$ must be taken to be complex. In this case, the middle term in Eq. (14) vanishes, because $\mathbf{E}_1\cdot\mathbf{E}_2=0$. The remaining terms are circularly co-polarized in the same direction as the input waves, allowing us to replace Eq. (14) with a scalar relationship:

$$J_{2+}=\sigma^{(1)}E_{2+}+\frac{3}{2}\sigma^{(3)}\frac{1+r}{1+2r}|E_{1+}|^2E_{2+} \tag{17}$$

The circular co-polarized case is expected to yield a somewhat weaker nonlinear response than the linear co-polarized case.

Now suppose the pump is right-handed circularly polarized (subscript +), but the probe is left-hand circularly polarized. In this case, the first and third nonlinear terms in Eq. (14) vanish, and the middle term is oppositely polarized to the pump wave (i.e., left-hand polarized). Again, because the resulting current is co-polarized with the probe, we can re-cast Eq. (14) as a scalar relationship between the field and current amplitudes:

$$J_{2-}=\sigma^{(1)}E_{2-}+\frac{3}{2}\sigma^{(3)}\frac{1}{1+2r}|E_{1+}|^2E_{2-} \tag{18}$$

We conclude that in an isotropic material, co-circularly polarized waves are predicted to produce the same pump-probe signal than oppositely circularly polarized waves, which is in contrast with the measurements.

d) <u>Simplification</u>

For simplicity, we can assume that r=1. In this case, we obtain the following relationships:

$$\mathbf{J}_2=\sigma^{(1)}\mathbf{E}_2+\frac{1}{2}\sigma^{(3)}[(\mathbf{E}_1^*\cdot\mathbf{E}_1)\mathbf{E}_2+(\mathbf{E}_1\cdot\mathbf{E}_2)\mathbf{E}_1^*+(\mathbf{E}_1^*\cdot\mathbf{E}_2)\mathbf{E}_1] \tag{19}$$

This leads to the following equations for linearly polarized radiation, in the co-polarized case:

$$J_{2x}=\sigma^{(1)}E_{2x}+\frac{3}{2}\sigma^{(3)}|E_{1x}|^2E_{2x} \tag{20}$$

and in the cross-polarized case:

$$\boldsymbol{J_{2y}}=\boldsymbol{\sigma^{(1)}E_{2y}}+\frac{\mathbf{1}}{\mathbf{2}}\boldsymbol{\sigma^{(3)}|E_{1x}|^2E_{2y}} \quad (21)$$

Remark: the optical Kerr effect for the cross-polarized case is expected to be smaller by a factor of 1/3 in comparison to the co-polarized case.

Circularly polarized radiation, co-polarized (+) and counter-polarized (-) case:

$$\boldsymbol{J_{2\pm}}=\boldsymbol{\sigma^{(1)}E_{2\pm}}+\boldsymbol{\sigma^{(3)}|E_{1+}|^2E_{2\pm}} \quad (22)$$

Remark: the circularly case is expected to be 1/3 smaller than for the linearly co-polarized case.

However, in all of the measurements, the response contains a slower thermal ($\boldsymbol{\sigma^{(1)}}$) contribution that is entirely polarization independent, so one cannot simply compare the magnitudes of the responses. Furthermore, as mentioned in the main text, the circular plasmons host effects that go beyond the here described Kerr nonlinearity.

References

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