



Making two-photon processes dominate one-photon processes using mid-IR phonon polaritons

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Phonon polaritons are guided hybrid modes of photons and optical phonons that can propagate on the surface of a polar dielectric. In this work, we show that the precise combination of confinement and bandwidth offered by phonon polaritons allows for the ability to create highly efficient sources of polariton pairs in the mid-IR/terahertz frequency ranges. Specifically, these polar dielectrics can cause emitters to preferentially decay by the emission of pairs of phonon polaritons, instead of the previously dominant single-photon emission. We show that such two-photon emission processes can occur on nanosecond time scales and can be nearly 2 orders of magnitude faster than competing single-photon transitions, as opposed to being as much as 8–10 orders of magnitude slower in free space. These results are robust to the choice of polar dielectric, allowing potentially versatile implementation in a host of materials such as hexagonal boron nitride, silicon carbide, and others. Our results suggest a design strategy for quantum light sources in the mid-IR/terahertz: ones that prefer to emit a relatively broad spectrum of photon pairs, potentially allowing for new sources of both single and multiple photons.

two-photon processes | phonon polaritons | light–matter interactions | Purcell effect | nanophotonics

A fundamental rule in light–matter interaction is that when an excited electron in an atom has a choice between emitting one photon and emitting two photons simultaneously, it will nearly always decay via the emission of a single photon (1–3). The reason for this is impedance mismatch, or equivalently, the mismatch in size between an emitter and its emitted radiation. Applying this idea to two-photon emission processes, one realizes that two-photon emission suffers much more from impedance mismatch than one-photon emission, leading to its relative suppression.

More quantitatively, the radiation resistance or impedance of a dipole radiator is proportional to $\sqrt{\frac{\mu_0}{\epsilon_0}} (a/\lambda)^2$, which up to other fundamental constants is proportional to $\alpha(a/\lambda)^2$ (4). It turns out that the radiation rate of an atomic dipole is precisely proportional to $\alpha(a/\lambda)^2$, where a is the atomic size, λ is the wavelength of the emitted light, and $\alpha \approx 1/137$ is the fine-structure constant. In contrast, the rate of a two-photon process scales as $\alpha^2(a/\lambda)^4$ (5–7) and suffers much more than the one-photon process when impedance is mismatched. In atomic systems, $(a/\lambda) \sim 1/1000$, and thus, two-photon emission in atoms is consistently slower than one-photon emission by more than eight orders of magnitude. It is because of this simple scaling argument that two-photon processes are considered insignificant and can thus almost always be ignored for the purposes of analyzing the dynamics of excited emitters. It is also because of this simple scaling argument that, while conventional (one-photon) spontaneous emission engineering is a paradigm in quantum nanophotonics (8–12), similar engineering has not been nearly as actively pursued for two-photon spontaneous emission processes (13–18).

Nevertheless, two-photon spontaneous emission processes have several distinctive features which make them very desirable to access. For example, the photons emitted in such a process are entangled due to energy and angular momentum conservation. For this reason, sources of entangled photons (such as spon-

taneous parametric down-conversion sources) have become a staple in quantum information protocols. From a more fundamental perspective, the frequency spectrum of two-photon spontaneous emission can be broad, with a spectral width of the order of the transition frequency itself. This is in sharp contrast to one-photon emission, which is spectrally very sharp in the absence of external broadening mechanisms. That implies that if two-photon processes were sufficiently fast, an emitter with discrete energy levels could be a source of light at continuous frequencies, which is in contrast to one of the first things that one learns about quantum mechanics.

In this work, we propose a design strategy for fast production of polariton pairs with quantum efficiencies potentially >90%. In other words, we propose a scheme in which an excited emitter prefers to decay via the simultaneous emission of two quanta, despite the possibility of allowed single-photon decay pathways. As a special case, we show how phonon polaritons (PhPs) in boron nitride and silicon carbide (SiC) may allow for the design of a kind of quantum optics source which emits polariton pairs at rates over an order of magnitude faster than any competing one-photon transitions, corresponding to lifetimes approaching 1 ns in atomic-scale two-photon emitters. Our results not only elucidate a technique for efficient sources of potentially entangled polariton pairs but also reveal a class of materials by which to realize extreme regimes of light–matter interactions in which conventionally unobservable high-order emissions become dominant light–matter interactions.

The general scheme for accessing high-efficiency second-order transitions is illustrated in Fig. 1. In free space (and near most

Significance

The recent discovery of nanoscale-confined phonon polaritons in polar dielectric materials has generated vigorous interest because it provides a path to low-loss nanoscale photonics at technologically important mid-IR and terahertz frequencies. In this work, we show that these polar dielectrics can be used to develop a bright and efficient spontaneous emitter of photon pairs. The two-photon emission can completely dominate the total emission for realistic electronic systems, even when competing single-photon emission channels exist. We believe this work acts as a starting point for the development of sources of entangled nano-confined photons at frequency ranges where photon sources are generally considered lacking. Additionally, we believe that these results add a dimension to the great promise of phonon polaritonics.

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nanophotonic structures), an emitter given a choice between different transition pathways will generally take a single-photon dipole (E1) transition over other choices. However, if we have highly confined modes (to impedance match) over a sufficiently narrow frequency band, then we can create a situation in which the single-photon E1 transition is negligibly enhanced, while the two-photon transition is highly enhanced (>10 orders of magnitude relative to the enhancement of the competing E1 transition), so much so that the two-photon transition is strongly preferred. As we will now demonstrate, one of the recent material advances that may admit the construction of such an emitter is the discovery of highly confined PhPs in polar dielectrics.

Polar dielectrics like hexagonal boron nitride (hBN) and SiC have been the subject of significant attention over the past few years due to their ability to confine electromagnetic energy in small volumes (length scales <5 nm have been theoretically suggested) (19–32). Moreover, the transversely guided PhPs of these materials have extremely strong spatial confinement only over a narrow spectral band of a few terahertz. Combined with the fact that these PhPs can have substantially lower losses than other surface excitations like plasmons (33) (albeit with lower velocities and similar propagation lengths), they may provide a potentially exciting platform for nanoscale optics in the technologically interesting IR/terahertz regime. Going beyond hBN and SiC, it should also be possible to exploit PhPs at mid-IR/far-IR frequencies in materials like cubic boron nitride (cBN), gallium phosphide, and many others (32). Much effort has been devoted to demonstrating the coupling and propagation of these modes. In this work, we focus on the potential of using the extreme local density of states (LDOS) in the vicinity of polar dielectrics to efficiently access a wide range of light–matter interactions. Before moving on to a quantitative description of the two PhP emission process considered here, we note that throughout the text, we use the terms “two-polariton emission” and “two-photon emission” interchangeably. This is because the PhP modes are described fully in terms of propagating modes of

Maxwell’s equations. The primary difference between them and free-space photons is that they are highly confined and cannot escape to spatial infinity in the direction transverse to the polar dielectric slab.

To translate our intuition to a quantitative theory, we develop a formalism to compute the rates of two-photon transitions for emitters placed near films supporting PhP modes (*Supporting Information*). Our main assumption is that these PhP supporting materials are well-described by a local Lorentz oscillator model (although we allow for the permittivity to be complex and anisotropic). Our permittivity data are taken from ref. 32. Agreement with a local model has been seen in hBN films as thin as 1 nm, although only the long-wavelength part of the dispersion was measured (20). Nevertheless, we will see that the results we arrive at should be achievable for thicknesses between 5 and 10 nm, and for polariton wavelengths of a few tens of nanometers, where a local model should certainly suffice.

Extreme LDOS Near Polar Dielectrics

The main operating principle behind our results is that the LDOS of the electromagnetic field in the vicinity of PhP supporting materials is extremely high. This LDOS can be so high that the emission rate of a dipole within nanometer distances from the surface of the material can be 6 or 7 orders of magnitude faster than in free space (i.e., the Purcell factor can be of order 10^6 to 10^7). Because the rate of emission of a pair of polaritons depends on two factors of the LDOS, the emission of pairs naively can be maximally enhanced by 12 or 13 orders of magnitude. Our detailed theory of two-photon emission into PhPs corroborates this intuition.

Although Purcell factors for one-photon emission have been predicted in ref. 31 in the context of SiC, and in ref. 9 in the context of hBN, we clarify the basic physics of why the LDOS is so high in the first place with transparent physical formulae, and show that Purcell factors $>10^6$ are to be expected. As is well

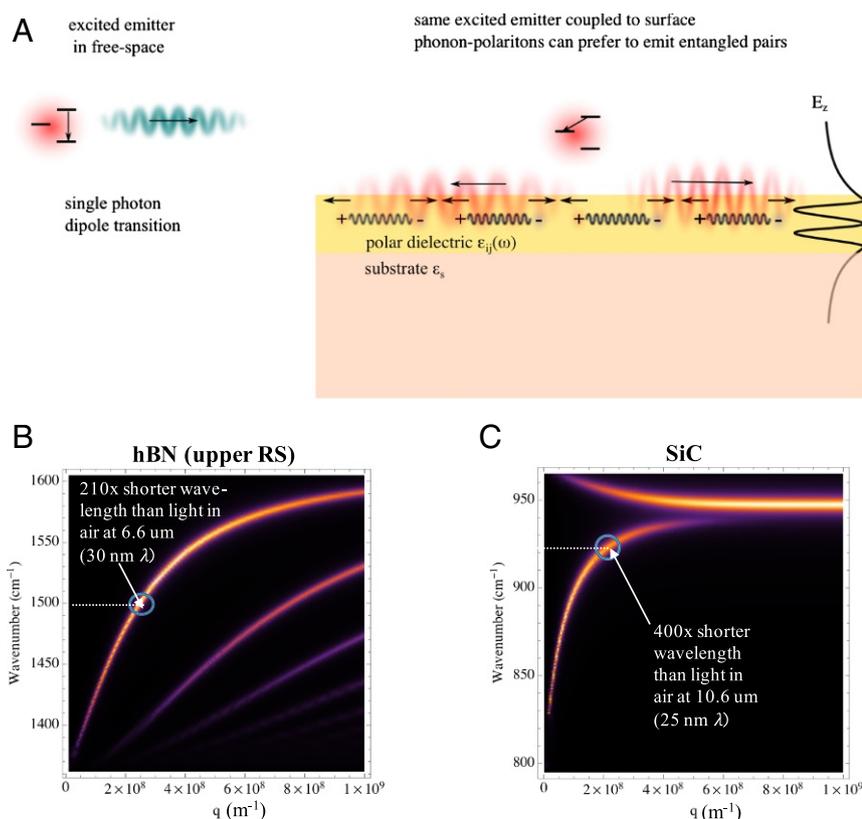


Fig. 1. General scheme for accessing two-photon transitions at high efficiency. (A, Left) Typical situation for an emitter: An emitter may have many choices for a transition, but the relatively high-frequency single-photon dipole transition is chosen. (A, Right) When coupling that same excited electron to PhPs in a polar dielectric, the electron can be made to prefer a two-polariton spontaneous emission. (B) Color plot of the imaginary part of the p-polarized reflectivity of 5-nm-thick hBN evaluated at the upper RS band. The center of the sharp peaks signify the dispersion relation. (C) Same for SiC in its sole RS band.

known, the spontaneous emission rate of an emitter in free space at frequency ω_0 (wavelength λ_0) goes like:

$$\Gamma_0 = \omega_0 \times \frac{4}{3} \alpha (k_0 a)^2, \quad [1]$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$ is the fine-structure constant, $k_0 = \frac{\omega_0}{c} = \frac{2\pi}{\lambda_0}$, and a is the emitter size. The dimensionless factor $\frac{4}{3} \alpha (k_0 a)^2$ is of order $10^{-7} - 10^{-9}$ for typical atoms and molecules and is indicative of the weak coupling between light and matter in free space. On the other hand, when the emitter is placed at a distance z_0 from a polar dielectric supporting PhP modes with polariton wavelength λ_{PhP} and group velocity v_g , the emission rate will scale like

$$\begin{aligned} \Gamma_{PhP} &\sim \omega_0 \times \frac{4}{3} \alpha_{PhP} (k_{PhP} a)^2 \exp\left[-\frac{4\pi z_0}{\lambda_{PhP}}\right] \\ &\sim \Gamma_0 \times \left(\frac{c}{v_g}\right) \times \left(\frac{\lambda_0}{\lambda_{PhP}}\right)^2 \exp\left[-\frac{4\pi z_0}{\lambda_{PhP}}\right], \quad [2] \end{aligned}$$

where $k_{PhP} = \frac{2\pi}{\lambda_{PhP}}$, $\alpha_{PhP} \equiv \frac{e^2}{4\pi\epsilon_0\hbar v_g}$, and we have omitted dimensionless factors that are $O(1)$.^{*} The exponential arises from the evanescent tails of these PhP modes, and the sharpness of those tails requires the emitter to be within ~ 10 nm from the surface of the polar dielectric. Assuming that indeed the emitter is in close enough proximity, the Purcell enhancement is governed by the factor $(k_{PhP} a)^2$, which is an impedance matching factor, and the factor $\left(\frac{c}{v_g}\right)$ which is a “slow-light” or density-of-states-enhancement factor. Since both of these properties can be easily gleaned from the dispersion relation of the PhPs, we now estimate the possible LDOS enhancements using the dispersion relations of SiC and hBN plotted in Fig. 1 B and C. As can be seen from the dispersion relations, the wavelength of the polariton can be >100 times shorter than the wavelength of light in free space. When the confinement factor is 100, the group velocity is well over 100 times slower than the velocity of light (due to the highly dispersive nature of these materials), and the corresponding Purcell factors for a sufficiently close emitter tend toward 10^6 . We emphasize that, although our result in Eq. 2 is just an estimate, we have calculated the Purcell factors using three approaches: a mode quantization approach assuming lossless polar dielectrics; a macroscopic quantum electrodynamics approach using dyadic Green’s functions, taking into account medium losses; and numerically in a finite-difference frequency-domain approach by placing a dipole emitter near polar dielectric surfaces. All three approaches are in agreement and corroborate the estimates provided here, lending support to all of the subsequent results.

To conclude this section, we briefly comment on the experimental state of the art. For substantially thicker films (of order 100-nm thickness), confinement factors >80 have already been observed in hBN associated with third-order modes, corresponding to polariton wavelengths of ~ 80 nm (34). Even larger wavelength confinements (up to 200) have been claimed in nanometric-scale SiC nanoresonators (31). In these SiC nanoresonators, the authors predicted on the basis of the measured quality factor and simulated mode volume a Purcell enhancement of about 10^7 . The theory we provide here is fully consistent with these find-

^{*}In ref. 33, it was suggested that perhaps the dimensionless factor could be much less than 1 as a result of the strong phononic character of the excitations, thus limiting the degree of enhancement. Being quantitative, one finds that this is not the case. Although most of the electromagnetic energy (incorporating the mechanical energy of vibrations) resides in the polariton sustaining slab, it is not much different from what happens in plasmonics, where most of the energy is inside the metal. Additionally, because of the dispersiveness of the polar dielectric, the group velocity becomes much less than the phase velocity, leading to a larger density of states enhancement than one would get in a comparable plasmonic system. This compensates for the strong phononic component of the excitations.

ings and predicts a potentially even greater degree of confinement for thinner slabs. That this effect is more visible for thinner films of polar dielectrics is because making the slab thinner pushes the dispersion toward higher wavevectors. A semiinfinite slab of such materials would have very weak confinement, as pointed out, for example, in ref. 25. All this said, an impediment toward experimentally observing even higher confinements comes from the limited resolution of scattering-scanning near-field optical microscopy techniques. Perhaps complementary approaches can make these extremely confined modes more visible.

Two-Photon Emission Enhancement Theory

Moving to two-photon emission, while there is no closed-form expression for the two-photon emission rate of a general emitter (because it depends on the detailed level diagram of the emitter), the emission rate in the absence of radiative cascades will generically scale as:

$$\Gamma_{0,2Ph} \sim \alpha^2 (k_0 a)^4 \Delta\omega \ll \Gamma_0, \quad [3]$$

where $\Delta\omega$ is the bandwidth of the two-photon emission spectrum. Note that in free space, it is generally of the order of half the transition frequency, but in the situations we consider, it is typically much less, leading to some suppression relative to what one might expect. The emission is into a continuum of frequency pairs $(\omega, \omega_0 - \omega)$ satisfying energy conservation. Such a result is corroborated by more detailed second-order perturbation theory calculations.

In the presence of a surface supporting PhPs, the rate of two-photon/two-polariton emission per unit frequency goes as (ignoring for now evanescent tails):

$$\frac{d\Gamma_{2PhP}}{d\omega} \sim \alpha_{PhP}^2 (k_{PhP} a)^4, \quad [4]$$

which, according to the estimates from the previous section would lead to enhancement of the emission spectrum of $\sim 10^{12}$ for an emitter sufficiently close to the surface. By virtue of Eq. 4, it follows that for PhPs with a bandwidth of $\sim 1/10$ of the transition frequency, the total rate enhancement is $\sim 10^{11}$. Going into a more rigorous level of detail, we show in *Supporting Information* that for an $s \rightarrow s$ transition, the spectral enhancement factor, defined as the ratio of the PhP emission spectrum, $\frac{d\Gamma}{d\omega}$, to the free-space emission spectrum $\frac{d\Gamma_0}{d\omega}$ is given by:

$$\text{Spectral Enhancement} = \frac{\frac{d\Gamma_{2PhP}}{d\omega}}{\frac{d\Gamma_{0,2Ph}}{d\omega}} = \frac{1}{2} F_p(\omega) F_p(\omega_0 - \omega), \quad [5]$$

where $F_p(\omega)$ is the Purcell factor for a dipole perpendicular to the surface. As is well known, the expression for the Purcell factor for a z-polarized dipole in the geometry of Fig. 1A is simply:

$$F_p(\omega) = \frac{3}{2k_0^3} \int dq q^2 e^{-2qz_0} \text{Im } r_p(q, \omega) \quad [6]$$

r_p is the p -polarized reflectivity of the air-slab-substrate system (plotted in Fig. 1 B and C), and $k_0 = \frac{\omega}{c}$ is the free-space photon wavevector (9, 35). We note that the two-photon spectrum is always symmetric with respect to reflection about half of the transition energy. This is because emission at $(\omega, \omega_0 - \omega)$ is indistinguishable from emission at $(\omega_0 - \omega, \omega)$.

Before turning to a discussion of our results, we discuss the validity of perturbation theory, which we use to arrive at the results above. The main result of this work is that two-phonon-polariton emission beats one-photon emission. Were it also the case that third- and higher-order emission processes were more important than second-order processes, it would be the case that our calculations based on second-order perturbation theory would not be representative of the full dynamics of the electron. We claim that this is not the case in our work and that two-photon emission dominates the perturbation series. An explicit estimate is provided in the final section of *Supporting Information*. To summarize those estimates, the only reason that two-polariton

of the emitter, given by $\frac{1}{\sqrt{2}}(\cos\theta, \sin\theta, i)$ in the high-confinement limit.

The angular dependence of the spectrum in Eq. 2 will lead to very different angular spectra for different transitions. In Table 1, we show the angular spectrum as a function of different transitions (at $\omega = \omega_0/2$). Strictly speaking, the angular spectrum is frequency-dependent. However, due to the narrowness of the RS band(s), this can be neglected, and thus we only consider the spectrum at half the transition frequency. Remarkably, just by changing the initial state of the system, one can change whether the polariton pairs are preferentially emitted in the same direction (as in Fig. 4, *Upper Right* and *Lower Left*) or in opposite directions (as in Fig. 4, *Upper Left*). There are a number of ways to preferentially populate a particular initial state. One is by exciting the atoms with light of a fixed polarization. Another, appropriate in systems with less extreme degeneracy than hydrogen, is to simply excite the atoms with the appropriate frequency.

Discussion

Although we have considered the hydrogen atom in our calculations, this was just for concreteness, and the physical mechanism for efficient two-photon emitters can readily be extended to many atomic and molecular systems. Here, we propose some emitter platforms for testing the predictions of our theory. For atoms, there are many which have a level structure conducive to the situation described throughout this paper. For example, in the lithium atom there is a $d \rightarrow s$ transition at $1,611 \text{ cm}^{-1}$, which can potentially occur via emission of a pair of PPs. All other competing transitions fall well outside of the RS bands of hBN, just as in the example we discussed in Fig. 2. More generally, as all atoms have electronic transitions in the mid-IR, our results should apply to a large portion of the periodic table. It may also be possible that vibrational transitions may be used to observe these effects, although one obstacle toward realizing these effects with molecular vibrations is the generally low multipole moments associated with vibrational transitions. Another exciting possibility is using emitters whose level structure is designable, such as quantum dots or wells. There, one can envision designing a two-photon transition to fall in the RS bands while

designing all other one-photon transitions to fall out of the band. Yet another advantage of these artificial atomic systems is their relatively large sizes, allowing for impedance matching to be realized which much less requisite polariton confinement.

In this work, we focused our attention on quantum optics at mid-IR/terahertz frequencies, a relatively undeveloped field, but nonetheless one which would be rather exciting to develop. Moving beyond the mid-IR to the near-IR and eventually visible, it may be possible to realize the effects we describe here using “shaped polaritonic media” (such as nanoresonators of graphene or plasmonic crystals of graphene and other 2D plasmonic materials) supporting (respectively) narrow spectral response or photonic bandgaps. We note that in all of these examples, the emitted quanta are confined modes and do not escape into the far-field unless outcoupled. Outcoupling efficiencies of a few percent were demonstrated in highly confined graphene plasmons, and even higher efficiencies should be demonstrable through optimization. We believe that the results presented in this work may have direct implications for spectroscopy (to infer electronic transitions which cannot be determined with conventional photons), sensors based on forbidden transitions, quantum radiation sources (on-demand generation of single photons and potentially entangled pairs of photons), new platforms for quantum nonlinear optics, the possibility of realizing nonlinearities at the single-photon level, the ability to turn narrow-band emitters into broadband emitters, the ability to turn narrow-band absorbers into broadband absorbers, and, most generally, the ability to completely reshape the ostensibly fixed optical properties of materials.

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