Anti-Stokes Excitation of Solid-State Quantum Emitters for Nanoscale Thermometry

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Abstract: We report the first demonstration of Anti-Stokes excitation on a single solid-state quantum emitter—namely the germanium-vacancy center in diamond and its application as a high-sensitive nanoscale thermal sensor. © 2019 The Author(s)

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1. Full Abstract

Stokes and Anti-Stokes emission are fundamental phenomena widely used to study the physico-chemical and optical properties of materials. Stokes (Anti-Stokes) photoluminescence (PL) occurs when the energy of the emitted photons is lower (higher) than that of the absorbed ones [1]. In the Anti-Stokes case, the extra energy that causes up-conversion of the photons can be acquired through a variety of mechanisms, ranging from multi-photon absorption to Auger recombination and phonon absorption. The latter, relevant to this work, is illustrated in Figure 1A, B. A photon with energy $h\nu_{exc}$ at the long-wavelength tail of the absorption spectrum excites an electron from a thermally-populated first vibronic state ($n_0 = 1$) of the electronic ground state E_0, to the bottom manifold ($n_1 = 0$) of an excited electronic state E_1 [red arrow]. The system then returns to the ground state via spontaneous emission of an up-converted photon with a mean energy $h\nu_{se} > h\nu_{exc}$ [yellow arrow]. This phonon-assisted Anti-Stokes excitation process scales exponentially with temperature and is the bedrock of a variety of fundamental studies (e.g. cavity quantum electrodynamics), as well as practical applications such as optical cryocooling, bioimaging and Raman spectroscopy. However, Anti-Stokes photoluminescence (PL) is inherently inefficient, and all work done to date on solid-state defects has been focused on ensembles [2-4] rather than individual point defects.

Here, we demonstrate that Anti-Stokes PL can be used to study isolated quantum systems—specifically atom-like color centers in diamond, over a large range of temperatures [5]. We explore the mechanism for some of the most studied diamond defects, the nitrogen-vacancy (NV) the silicon-vacancy (SiV) and the germanium-vacancy (GeV) center. We show that Anti-Stokes excitation of selected diamond color center is an efficient process, detectable by standard photoluminescence spectroscopy and leverage this finding to demonstrate upconversion PL from a single, isolated GeV defect. We show that the Anti-Stokes excitation process is thermally-activated and proceeds through a phonon-photon absorption pathway rather than through multi-photon absorption. We exploit the high Anti-Stokes excitation efficiency to introduce an innovative approach for all-optical nanoscale thermometry based on the temperature-dependence of the Anti-Stokes to Stokes PL intensity ratio. Our technique outperforms all other previously reported all-optical nanothermometry methods.
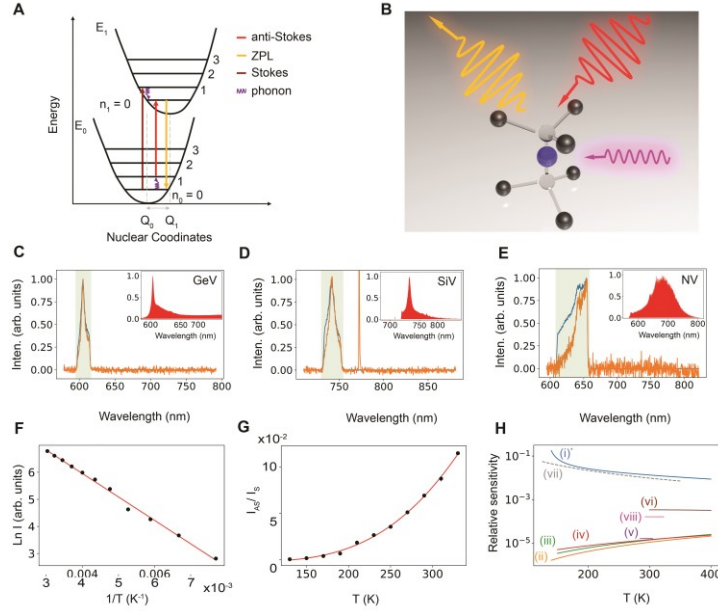
Fig. 1 Stokes and Anti-Stokes luminescence processes for color centers in diamond. (A) Energy diagram of representative electronic and vibrational energy levels for a diamond color center. The arrows show the lower (higher) energy of the Stokes (Anti-Stokes) photons with respect to the ZPL energy. In the Anti-Stokes case, the additional energy is acquired via phonon(s) absorption. (B) artistic representation of the Anti-Stokes mechanism for a diamond color center which absorbs a lower-energy photon [wavy line, red] and emits a higher-energy one [wavy line, ocher] upon absorption of a phonon [wavy line, purple]. (C–E) Photoluminescence spectra of the ZPL for nanodiamond GeV (C), SiV (D) and NV (E) centers under Stokes [blue] and Anti-Stokes [ocher] excitation (the full PL spectrum under Stokes excitation is shown in the relative inset). The ZPLs (605 nm for GeV, 739 nm for SiV and 639 nm for NV) are spectrally filtered by means of bandpass filters (semitransparent rectangular boxes). Characterization of the Anti-Stokes GeV-based nanothermometer. (F) Temperature dependence of the PL intensity signal upon Anti-Stokes excitation (637-nm wavelength). The PL intensity was measured by monitoring the GeV's ZPL (605 nm) isolated with a bandpass filter. The data fit well the Arrhenius-type equation $Ae^{-(E_a/k_BT)}$, where the activation energy E_a = 102.96 meV is fixed to coincide with the difference in energy between the excitation laser and the germanium-vacancy's ZPL. (G) Plot of the Anti-Stokes to Stokes PL ratio as a function of temperature. The ratio fits an exponential curve: $a + be^{-[c/(T-T_0)]}$, granting the method an extremely high sensitivity. The error bars of plots in (F) and (G) are represented as vertical, blue bars, and are mostly equivalent to or smaller than the size of the data points. (H) Relative sensitivity plotted vs temperature for several different systems: our $I_{AS}/I_S|_{GeV}$ measurement *(i)**, the frequency of the GeV ZPL in our Stokes PL spectra *(ii)*, and the equivalent measurement from the literature *(iii)*, the ZPL wavelength shift of the SnV *(iv)* and of the SiV center *(v)*, the intensity of the NV ZPL *(vi)*, the Raman I_{AS}/I_S ratio achieved for a bulk thermometer *(vii)* and the spectral shift of quantum dots *(viii)*. The literature data are plotted over the entire temperature range demonstrated in each paper.

2. Summary

In conclusion, we present the first demonstration of Anti-Stokes excitation on a single solid-state quantum emitter—namely the germanium-vacancy center in diamond and its application as a high-sensitive nanoscale thermal sensor.

3. Acknowledgements

4. References

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