to a conductance plateau with an integer number $N$ of fully transmissive ($T = 1$) modes. Experimental details are given in ref. 7.

The deviations from the quantum limit $^{1}\chi F = 1/4$ towards the regime of deterministic scattering $F < 1/4$, described by equation (3), are explored by changing $\tau_D$. This dwell time depends on the area $A$ of the cavity and the conductances $G_{L,R}$ of the contacts:

$$\tau_D = \frac{2e^2 m}{\pi h^2 (G_L + G_R)}$$

(4)

In a first experiment we changed the openings (conductances) of the contacts to alter $\tau_D$. In Fig. 3a, the Fano factor $F$ of a symmetric ($N_L = N_R$) cavity is plotted as a function of the inverse dwell time $\tau_D^{-1}$ for four different settings ($N_L = 5$, $14$, $22$ and $40$). The left inset shows the measured shot noise for $N_L = N_R = 5$. As the contacts were further opened and the dwell time was subsequently reduced, the shot noise was observed to decrease. The Fano factor $F$ shows a pronounced decay below the quantum limit $1/4$. A linear fit of the data to equation (3) yields a $\tau_D$ of 270 ps. We emphasize that the total resistance $R$ equals the series resistance $R_L + R_R$ of the two contacts within the measurement accuracy of $\sim 3\%$ (Fig. 3b).

Hence, the shot noise measurements are carried out in a regime where the direct (ballistic) transmission of electrons from the left to the right contact can be neglected. The suppression of shot noise observed here is a consequence of reduced diffraction, and serves to demonstrate that shot noise disappears in the limit of purely classical scattering.

An alternative way to change $\tau_D$ is to apply a perpendicular magnetic field. Because a magnetic field forces the electrons onto circular orbits with the cyclotron radius $R_c = m v_F / B$ (where $m$ denotes the electron mass and $v_F$ the Fermi velocity), the dwell time $\tau_D$ will be reduced with increasing magnetic field $B$ provided that $R_c < L$. An annulus of skipping orbits is formed (Fig. 4b inset) in which transport takes place. Such an annulus represents a ‘new’ (and smaller) chaotic cavity inside the actual cavity. For low magnetic fields (large filling factors), the electron dynamics inside the annulus can still be considered to be random (because of imurities or irregularities in the geometry of the cavity). Thus equations (2) and (3) are still valid with the area $A$ in equation (4) replaced by $A = 2\pi L_c$, where $L_c \approx L$ is the circumference of the cavity. This leads to $\tau_D \approx B$.

Figure 4b shows the measured Fano factor $F$ as a function of inverse dwell time $\tau_D^{-1}$ in a magnetic field. We again observe a very marked reduction of $F$ with increasing $\tau_D^{-1}$, while the total resistance $R$ approximately equals the series resistance $R_L + R_R$ of the two contacts in lower fields ($B < 1.2T$) (Fig. 4a). A linear fit (equation (3)) results in a quantum scattering time $\tau_D^{-1}$ of $\approx 485$ ps, which is in qualitative agreement with $\tau_D$ obtained from the measurements in zero field. If the magnetic field is further increased beyond 1.2T, the ratio $R/(R_L + R_R)$ starts to deviate from unity and equals 1/2 at the highest magnetic field. Here, we enter a new regime in which a significant fraction of electrons is ballistically transmitted from source to drain. The last measurement point in Fig. 4 with $F = 0$ and $R/(R_L + R_R) \approx 0.5$ corresponds to the integer quantum Hall regime with filling factor four, where the electrons propagate within ballistic edge states.

Received 8 August; accepted 12 December 2001.


Acknowledgements

We thank H. Büttiker and H. Thomas for discussions. This work was supported by the Swiss National Science Foundation.

Correspondence and requests for materials should be addressed to C.S. (e-mail: Christian.Schoenenberger@unibas.ch).

---

**Observation of stimulated emission by direct three-photon excitation**

Guang S. He, Przemyslaw P. Markowicz, Tzu-Chau Lin & Paras N. Prasad

Institute for Lasers, Photonics and Biophotonics, University at Buffalo, The State University of New York, Buffalo, New York 14260-3000, USA

Multiphoton processes, predicted theoretically in 1931, were for a long time considered to be mainly of academic interest. This view changed when it was shown that a two-photon absorption process could, because of a quadratic dependence of excitation on intensity, produce a spatially confined excitation useful for three-dimensional data storage and imaging. Two-photon absorption has received considerable attention recently because of the development of highly efficient two-photon-sensitive materials, leading to numerous technological applications. These successes have created interest in exploring applications based on three-photon excitations. For a three-photon process, a longer excitation wavelength such as those common in optical communications can be used. Also, the cubic dependence of the three-photon process on the input light intensity provides a stronger spatial confinement, so that a higher contrast in imaging can be obtained. Here we report the observation of a highly directional and up-converted stimulated emission as an amplified spontaneous emission, produced in an organic chromophore solution by a strong simultaneous three-photon absorption at 1.3 $\mu$m. This achievement suggests opportunities for a three-photon process in frequency-upconversion lasing, short-pulse optical communications, and the emerging field of biophotonics.

In our experiment, the gain medium is the organic chromophore 4-[(2-hydroxyethyl)N-(methyl)amino phenyl]-4’-(6-hydroxy-hexyl sulphonyl) stilbene (APSS) dissolved in dimethyl sulphoxide (DMSO). APSS has been reported to exhibit good properties for two-photon pumped lasing as well as for optical power limiting, when excited at a wavelength of $\sim 800$ nm. The molecular structure of APSS and its linear absorption spectrum in DMSO were shown in our previous publications. We report here that APSS also exhibits a strong three-photon absorption when excited by ultrashort laser pulses at $\sim 1.3$ $\mu$m, producing population inversion. This creates the prospect of developing new three-photon materials with even more enhanced cross-sections for three-photon absorption. Our
1.3-micron harmonic generation (SHG) produced separately from a BBO crystal excited with the same 1.3-micron wavelength of visible emission, pumped by three-photon absorption.

In our experiment, a 1-cm-long quartz cuvette filled with an APSS/DMSO solution of concentration 0.06 mol l\(^{-1}\) was employed as the gain medium. A laser beam of high peak power and 150-fs-duration, focused 0.55-micron wavelength laser output, with a spectral width of ~8 nm, and at a repetition rate of 1 kHz. The APSS molecules in solution have no linear absorption in the spectral range from ~500 nm to ~1.3 microns. But when illuminated by the focused 1.3-micron laser beam, an obvious yellowish-green fluorescence can be readily observed from any direction, which implies a frequency-upconversion emission process, induced by three-photon absorption. Furthermore, once the intensity level of the input laser beam is increased above a certain threshold value, a highly directional coherent emission of ~0.55 microns can be observed in both the forward and the backward directions. Figure 1a shows the intense and highly directional forward stimulated emission of 0.55-micron wavelength from the APSS solution cell; Fig. 1b shows second-harmonic generation (SHG) when the same 1.3-micron pump beam passes separately through a beta barium borate (BBO) crystal.

These two are shown together for comparison of their beam coherence properties. The spectral and temporal properties of this coherent three-photon excited emission in both forward and backward directions are basically identical, and not dependent on the incident angle (from 0° to ~10°) of the pump beam on the sample cuvette. These facts exclude the possibility that the observed directional emission is due to continuum generation, because the latter is not expected in the backward direction.

Figure 2 shows the spectral structures of the three-photon-induced spontaneous fluorescence measured at ~90° direction with respect to the pump beam, as well as of the forward and backward frequency-upconverted stimulated emission. It also shows the spectral characteristics of the second harmonic of the pump laser beam, which was generated by an external BBO crystal and could be used to determine the exact pump wavelength. From this figure we can see that the central wavelengths of the coherent visible emission in both directions are nearly the same, and located at ~553 nm with a spectral width of ~10 nm (full-width at half-minimum) that is about 8.5 times narrower than the corresponding fluorescence spectrum. From the peak position of the SHG signal of the pump beam, the central wavelength of the pump light is determined to be 1.292 nm.

Figure 3a–c shows temporal profiles of the pump laser pulse, the forward up-conversion coherent emission, and the ~90° fluorescence emission, respectively. These profiles were measured utilizing a high-speed streak camera (C5680-22 from Hamamatsu) with a resolution of ~2 ps for Fig. 3a and b, and ~20 ps for Fig. 3c. Two features can be seen from this figure. First, there is a delay between the input pump pulse and the stimulated emission pulse, and...
second, the pulse duration of stimulated emission is much longer (about 30–50 ps) than the pump pulse. The delay in emission may reflect an equivalent relaxation time of APSS molecules from their higher (three-photon) excited states to the emitting lower relaxed state. From the observed temporal behaviour of the visible coherent emission, the possibility of coherent emission from stimulated scattering and four-wave-mixing processes can be excluded, as these processes would not produce any overall delay or temporally broadened emission with respect to the pump pulse.

As shown in Fig. 3c, the average fluorescence lifetime, determined from the side emission of the cuvette, is ~720 ps. The forward coherent emission, therefore, shows a considerable temporal narrowing, a gain characteristic of stimulated emission. Cavity feedback is not possible in our case because of the use of ultrashort pump pulse, so what we observed is a highly directional amplified spontaneous emission.

The suggested energy level structure and the simultaneous three-photon absorption pathway for our chromophore are shown in Fig. 4. The population inversion is created between the lower emitting state, $S_1$, and the ground state, $S_0$. To demonstrate the high directionality of the stimulated emission, the transmitted pump laser beam and the forward stimulated emission beam were recollimated through a lens, and then projected on a paper screen. Images of these two beams on the screen could be recorded separately by a charge-coupled device (CCD) camera in conjunction with appropriate filters. We find that these two beams (also including the backward coherent emission beam) have nearly the same spatial profiles.

On the basis of these results—that is, the remarkable spectral narrowing, high directionality, temporal delay, and a relatively longer emission pulse compared to the pump pulse—we conclude that the observed coherent visible emission is a single-pass stimulated emission in the form of amplified spontaneous emission.

**Figure 3** Streak-camera measurements. Temporal profiles of the 1.3-μm pump pulse (a), the transmitted pump pulse together with the 553-nm forward stimulated emission (b), and the three-photon-induced fluorescence emission (c). In c, the lifetime of the fluorescence is ~720 ps.

**Figure 4** Diagram showing the proposed mechanism for three-photon excitation and stimulated emission. $S_i$ is a higher singlet (electronic or vibronic) state; $S_j$ is the radiative lower singlet state; $S_k$ is the ground state. Under our experimental conditions, a transient population inversion is created between $S_j$ and $S_k$.

**Figure 5** Output/input characteristics of three-photon-pumped stimulated emission. a. Transmission change induced by three-photon absorption versus input intensity of 1.3-μm radiation. $\gamma = 0.5 \times 10^{-4}$ cm$^2$ GW$^{-2}$, $z = 1$ cm (see text for definitions). b. Pump intensity depletion versus input intensity. c. Output optical energy versus the pump energy.
derived from population inversion of the excited chromophore molecules, produced by a simultaneous three-photon absorption process. The nonlinear transmissivity of a three-photon absorbing medium can be written as

$$T' = \frac{1}{l_0} \frac{1}{\sqrt{1 + 2gzI_0^2}}$$

(1)

where $l_0$ is the input light intensity, $z$ is the propagation distance in the medium, and $\gamma$ is the three-photon absorption coefficient of the medium.

From equation (1), the $\gamma$ value for a given sample medium can be experimentally determined by measuring the nonlinear transmission at a given input intensity level. In our case, at a pump level of ~190 GW cm$^{-2}$, the $\gamma$ value is evaluated to be 0.5 (±15%) × 10$^{-15}$ cm$^2$ GW$^{-2}$ for the APSS/DMSO solution of $d_0 = 0.06$ mol l$^{-1}$. On the basis of this value, we can predict the theoretical curve of nonlinear transmission $T'$ of the pump beam versus its intensity change (Fig. 5a). The depletion of pump intensity (or energy) due to three-photon absorption is determined by $I_0(1-e^{-\gamma z I_0^2})$, and is shown in Fig. 5b. It may be assumed that the stimulated emission is proportional to the absorbed pump energy. The measured values of pulse energy of the overall (forward and backward) visible stimulated emission as a function of the input pump energy are shown in Fig. 5c. These experimental data were obtained at two different repetition rates for the pump pulses, while a beam-chopper was employed in the low-repetition-rate case. In Fig. 5c, the solid fitting curve is obtained directly from Fig. 5b after a simple re-scaling of the $y$ axis. The agreement between the experimental data and the fitting curve seems to support the three-photon absorption model. As shown in Fig. 5c, at the pump level of ~1.5 μJ, the optical output energy was ~17 nJ, with an overall energy conversion coefficient of ~1.1%. At this pump level, the measured nonlinear transmission was ~0.47; therefore, the net conversion coefficient from the absorbed pump energy to the output energy would be ~2.1%.

Efficient three-photon absorption at 1.3 μm could be useful for short-pulse optical fibre communications, as it could be used for wavelength shifting, pulse reshaping and stabilization. Because the 1.3-μm radiation also provides a greater penetration into biological tissues and is less damaging to the cells than the visible-wavelength radiation, an efficient three-photon absorption at 1.3 μm as reported here could also provide opportunities in biophotonics, such as bioimaging and light-activated therapy at deep levels in tissues.

Acknowledgements

This work was supported by the US Air Force Office of Scientific Research, Washington DC, and the Polymer Branch of the US Air Force Research Laboratory at Dayton.

Competing interests statement

The authors declare that they have no competing financial interests.

Correspondence and requests for materials should be addressed to P.N.P. (e-mail: pnprasad@acsu.buffalo.edu).

Why stainless steel corrodes

Mary P. Ryan†, David E. Williams†, Richard J. Chater†, Bernie M. Hutton† & David S. McPhail‡

† Department of Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK
‡ Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Stainless steels are used in countless diverse applications for their corrosion resistance. Although they have extremely good general resistance, they are nevertheless susceptible to pitting corrosion. This localized dissolution of an oxide-covered metal in specific aggressive environments is one of the most common and catastrophic causes of failure of metallic structures. The pitting process has been described as random, sporadic and stochastic and the prediction of the time and location of events remains extremely difficult. Many contested models of pitting corrosion exist, but one undisputed aspect is that manganese sulphide inclusions play a critical role. Indeed, the vast majority of pitting events are found to occur at, or adjacent to, such second-phase particles. Chemical changes in and around sulphide inclusions have been postulated as a mechanism for pit initiation but such variations have never been measured. Here we use nanometre-scale secondary ion mass spectroscopy to demonstrate a