Room-temperature quasi-continuous-wave pentacene maser pumped by an invasive Ce:YAG luminescent concentrator

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We present in this work a quasi-continuous-wave (CW) pentacene maser operating at 1.45 GHz in the Earth’s magnetic field at room temperature with a duration of ~4 ms and an output power of up to -25 dBm. The maser is optically pumped by a cerium-doped YAG (Ce:YAG) luminescent concentrator (LC) whose wedge-shaped output is embedded inside a 0.1% pentacene-doped para-terphenyl (Pc:Ptp) crystal. The pumped crystal is located inside a ring of strontium titanate (STO) that supports a TE_{015} mode of high magnetic Purcell factor. Combined with simulations, our results indicate that CW operation of pentacene masers at room-temperature is perfectly feasible so long as excessive heating of the crystal is avoided.

I. INTRODUCTION

The maser[1], the microwave analogue of a laser, is a device that exploits stimulated emission to amplify electromagnetic signals at GHz frequencies with very little added noise. By offering extreme sensitivity (i.e., noise temperatures of just a few Kelvin)[2], exceptionally low intermodulation distortion[3], and rock-solid durability (in the face of jamming or accidental input overload), solid-state masers[4, 5] have proven themselves useful for device that exploits stimulated emission to amplify electromagnetic signals at GHz frequencies with very little added noise. By offering extreme sensitivity (i.e., noise temperatures of just a few Kelvin)[2], exceptionally low intermodulation distortion[3], and rock-solid durability (in the face of jamming or accidental input overload), solid-state masers[4, 5] have proven themselves useful for time keeping and metrology[9, 10]. It was noted early on[11] that zero-field masers, though not magnetically tunable, dispense with the need for carefully grown monocrystals of known cut and orientation.

In the case of solid-state gain media like ruby (based on covalently or ionically bonded crystals), the rapid increase in the rate of spin-lattice relaxation with absolute temperature makes room-temperature operation challenging, thus motivating the exploration of different materials and pumping schemes. In 2012, an optically-pumped solid-state maser based on pentacene-doped para-terphenyl (Pc:Ptp), operating at 1.45 GHz, was demonstrated[12], though maser oscillation occurred in bursts lasting only ~250 μs. Despite providing a high polarization density and thus high instantaneous output power (of around -10 dBm), it was suspected that “bottlenecking”[13] in the material’s spin dynamics prevented this maser from operating in continuous wave (CW) mode, thus fueling a search for alternatives[15–17]. Though a breakthrough came with the demonstration of a room-temperature maser employing nitrogen-vacancy (NV−) defects in diamond[18] that was capable of CW operation, it required a uniform applied magnetic field of ~ 430 mT and saturates at a vastly lower output power (~90 dBm). As was already pointed out in ref. [13], low-noise amplification at room temperature requires that the maser’s co-operativity (η in ref. [13], or C in ref. [18] and this work) must vastly exceed unity. In other words, the “cold” active gain provided by the maser’s pumped medium must substantially outstrip the “warm” passive losses incurred through dissipation within the maser’s electromagnetic cavity. Since no published NV− diamond maser has yet operated in this regime, the potential of such masers to amplify more quietly (i.e, demonstrate lower noise temperatures) than conventional HEMT-based microwave amplifiers remains unproven. The high doping concentrations (parts per thousand) and thus high spin-polarization densities that Pc:Ptp provides (together with usefully long decay/decoherence times) offers hope of accessing the elusive “C ≥ 1” regime needed for low-noise amplification at room temperature, as well as a route to the realization of strong-coupling effects[19].

Recently, we accurately investigated the zero-field spin dynamics of the (lowest lying) triplet state of pentacene when doped in para-terphenyl at room-temperature[20] and found the dynamics to lie tantalizingly close to the boundary between the “bottlenecked” and ”CW-masing-feasible” (C ≥ 1) regimes. Encouraging results with pump pulses of longer duration motivated us to re-examine the feasibility of CW operation. In this paper, we present a room-temperature pentacene maser working in a quasi-continuous wave mode (quasi-CW) with an output power up to -25 dBm and a duration of ~4 ms. This duration was as long as that of the optical pulse pulse applied to the gain medium. We attribute this accomplishment to three key modifications over the original pentacene maser: i) the use of a different optical pump source, ii) improved optical coupling of the pump light into the maser crystal and iii) the use of a maser cavity supporting a microwave mode of high magnetic Purcell factor. Unlike conventional optical pumping with pulsed lasers[12, 14], we use a cerium-doped YAG luminescent concentrator (Ce:YAG LC) pumped by a xenon flash lamp[21]. This source can provide intense pulses of yellow light substantially longer in duration than what a long-pulsed dye laser can generate. Instead of pumping the maser crystal through its exterior surface, the
Ce:YAG LC with wedged output faces was embedded into the Pc:Ptp crystal, thus implementing what we refer to as “invasive optical pumping”[22]. This considerably improves the illumination of the crystal throughout its bulk and avoids thermal damage (scorching) at the crystal’s surface. Moreover, a miniaturized maser cavity made of a strontium titanate (STO) crystal was employed to boost the spin-photon coupling (i.e., Einstein’s $B$ co-efficient) via the Purcell effect[23], thus lowering the optical pumping threshold[24]. By simulating the obtained 4-ms maser burst obtained experimentally, we found that pentacene’s underlying spin dynamics supports CW maser operation at room-temperature, provided the heat dissipated within the maser crystal by optical pumping can be removed.

II. PRINCIPLE OF MASER OPERATION – TRIPLET MECHANISM

The pentacene maser is pumped through the triplet mechanism (“TM”) as shown in Fig. 1. Individual pentacene molecules substitutively doped into the para-terphenyl crystal are optically pumped from the singlet ground state $S_0$ to the singlet excited state $S_i$ ($i = 1, 2, 3, \ldots$) for which the pump wavelengths of 590 nm, 550 nm and 510 nm have been determined to be optimal (and hence spin polarization) across $T_1$’s sublevels. This provides the prerequisite condition for masing: a strong initial population inversion across $|X\rangle$ and $|Z\rangle$. When the highly polarized pentacene molecules are placed in a cavity supporting a microwave mode at 1.4495 GHz, which matches the zero-field splitting between $|X\rangle$ and $|Z\rangle$, stimulated emission is induced by microwave photons occupying the mode. Alongside stimulated emission, spin-lattice relaxation and non-radiative decay of triplets back to $S_0$ affect the populations of the three sublevels of $T_1$. Masing occurs when the gain associated with stimulated emission (minus the loss associated with stimulated absorption across the same $|X\rangle \leftrightarrow |Z\rangle$ transition) exceeds the dissipative decay rate for 1.45 GHz photons in the mode.

III. MASER ASSEMBLY

The experimental setup of the quasi-CW pentacene maser is shown in Fig. 2 with all critical components labelled. Salient details about the maser assembly are described below.

A. Optical pumping

A luminescent concentrator (LC) was received from Crytur[27] in the form of a slender bar (rectangular prism) of “Cryphosphor”-branded Ce:YAG; its dimensions were 80 mm long ($l \times 5$ mm wide ($w \times 0.6$ mm thick ($d$) with all six of its faces polished. Additional...
faces were then flat-ground and polished by hand onto one end of the bar. These faces comprised (i) one wide isosceles-trapezoidal face reducing the bar’s thickness and (ii) a symmetrical pair of narrow triangular faces reducing the bar’s width. The latter allowed the wedged end to fit into the 4-mm bore of the maser cavity’s STO dielectric ring (see Fig. 3). The LC’s outputting faces, injecting light into the crystal, comprised the above three faces plus the section of the bar’s untouched \( l \times w \) face lying opposite the trapezoidal face (i). To maximise the output at the wedged end, the \( w \times d \) face at the opposite end of the Ce:YAG bar was attached to a small solid-silver mirror, which reflected light back into the bar towards its wedged end.

Optical characterisations in terms of the absorptive and emissive properties of the xenon flash lamp, Ce:YAG LC and 0.1% Pc:Ptp crystal were carried out to verify the feasibility of the optical pumping scheme. Optical absorption spectra of the Ce:YAG LC and Pc:Ptp crystal were measured by an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The photoluminescence (PL) of the Ce:YAG LC was measured by a Horiba Fluorolog-3 spectrophotometer, exciting at 410 nm (this choice of excitation wavelength avoided saturating the instrument’s sensitive photo-multiplier detector). The emission spectrum of the xenon flash lamp was measured by coupling light from the fused-silica waveguide’s output face into the input aperture of a home-made integrating sphere [21]: light from the output aperture of the sphere was fed into an Ocean Optics USB2000+ spectrometer. The emission and absorption spectra obtained from the above measurements are shown together in Fig. 4. With the glass band-pass filter in place, the output of the xenon flash lamp shows a broad peak ranging from 350 nm to 800 nm indicating the effective elimination of ultraviolet and infrared light together with a good spectral match to Ce:YAG’s visible absorption band in the blue, peaking at \( \sim 460 \) nm. The measured emission from the Ce:YAG luminescent concentrator ranges from 480 nm to 700 nm and overlaps with the transition wavelengths of \( S_0 \rightarrow S_1 \) (590 nm), \( S_0 \rightarrow S_2 \) (540 nm) and \( S_0 \rightarrow S_3 \) (510 nm) for pentacene molecules within the Pc:Ptp crystal, which implies that a Ce:YAG LC should work as an effective, albeit imperfect, pump source for pentacene masers. It is worth noting that although the emission spectrum of the xenon flash lamp also overlaps with the pentacene’s absorption bands, the LC’s prismatic geometry and specular surfaces, as shown in Figs. 2 and 3, substantially eliminate any direct pumping of the Pc:Ptp crystal by the xenon flash lamp, ensuring that all the light absorbed by pentacene molecules within the Ptp crystal derives from the Ce:YAG’s luminescence.

The Ce:YAG LC was pumped by a xenon lamp housed within the water-cooled output head of a Lumenis Vasculight intense-pulsed-light (“IPL”) source designed for aesthetic skin treatments. Light from the head was conveyed to the LC via a polished fused-silica waveguide (supplied by Robson Scientific; 150 mm long \( \times \) 34 mm wide \( \times \) 8 mm thick); its outputting end face was stationed \( \sim 2 \) mm from one of the LC’s 5-mm-wide faces. A glass band-pass filter transmitting wavelengths between 350 nm and 800 nm (inset of Fig. 2) was installed between the glass flow tube (containing the xenon lamp) of the IPL’s head and the waveguide’s input face. This guaranteed that no harmful ultraviolet light could escape from the IPL head, and reduced the unnecessary heating of the LC by infrared light from the lamp’s hot xenon plasma.

**FIG. 3.** Concept and design of the invasive optical pumping with the wedged Ce:YAG LC. (a) Photograph highlighting the original and wedged output faces of the Ce:YAG LC under room light. (b) Schematic of the wedged Ce:YAG LC with its dimensions. With optical pumping, the induced luminescence (green lines) escapes the LC from its wedged output faces.

**FIG. 4.** UV/Vis spectra of Ce:YAG (grey) and Pc:Ptp (purple) and emission spectra of Ce:YAG (orange) and xenon flash lamp (cyan).
B. Gain medium

The maser gain medium was a para-terphenyl (PtP) crystal substitutionally doped with pentacene (Pc) molecules at a molar ratio of 0.1% (nominal). Using the vertical Bridgman-Stockbarger method, this crystal was grown around the wedged end of the Ce:YAG bar to form a “lollipop”, with the wedge functioning as an internal mould (see Figs. 5(b) & (c)). Pentacene (TCI Europe NV) was used as received and para-terphenyl (Sigma-Aldrich, ≥99.5%) was purified by zone-refining with 30 cycles. Both were finely ground into powder and mixed in the molar ratio of 1 : 1000. The mixture was loaded into a small clean borosilicate tube (inner diameter (I.D.) ∼5.5 mm). A cylindrical poly-tetrafluoroethylene (PTFE) sleeve with an inner diameter of 4 mm and a height of 8 mm was fitted around the wedged end of the LC. This sleeve acted as an external mold limiting the crystal’s radial growth to the same diameter. Several bent layers of PTFE film were gently wedged between the LC and the lip of the small borosilicate tube; these prevented the LC from sliding downwards during the crystal’s growth. The tube containing the mixed powder, the LC and the PTFE sleeve was lowered into a larger borosilicate tube (Dixon Science, 9 mm I.D., already flame-sealed at its bottom end) which was then flame-sealed at its top end under an argon atmosphere (BOC, 99.9999%, ∼800 mbar pressure). The entire assembly is shown in Fig. 5(a). The sealed outer tube was dangled by a nichrome wire from the end of a cantilever attached to the translation stage of a home-constructed vertical translator. It was then lowered into a vertical tube furnace (Elite Thermal Systems Ltd.) with the tapered end of the smaller internal borosilicate tube positioned at the furnace’s central (hottest) zone, set to a temperature of 217 °C (just sufficient to melt the mixed powder). Using the vertical translator, the vial was lowered towards a cooler part of the tube furnace at a rate of 2 mm per hour. Once it was certain that the whole melt had re-solidified (by knowing the furnace’s vertical temperature profile), the oven’s temperature was ramped downwards at the rate of ∼10 °C per hour. A nominally 0.1% Pc:PtP crystal was thereby formed around the wedged end of the Ce:YAG LC after a 3-day growth and cooling run. Cracking away the outer and inner borosilicate tubes, then carefully peeling away the inner PTFE sleeve, left a pink cylindrical bead of Pc:PtP crystal on a prismatic, lemon-yellow shank of Ce:YAG. The wedged output faces of the Ce:YAG luminescent concentrator were entombed within the bead; this resulted in the “lollipop” as shown in Figs. 5(b) and (c). The bead of Pc:PtP fitted snugly into the STO ring shown in Fig. 2.

By growing the Pc:PtP crystal on the wedged end of the LC, the LC’s guided phosphorescence can be “injected” efficiently into the bulk of the crystal; this is the aforementioned “invasive optical pumping” approach[22]. This approach is uniquely available to optically-pumped masers since, in contrast to a laser crystal, the optical homogeneity of the gain medium matters. Optical-supply waveguides (acting like “arteries” for light flow) of a different refractive index to the maser gain medium itself (such as the wedge inserted within the Pc:PtP bead) can advantageously (w.r.t. pumping) invade the gain medium without adversely affecting the “beam quality” of the electromagnetic wave being amplified. The only downside of using these supply arteries is that the space they occupy could otherwise be filled with gain medium; in other words, the maser crystal’s filling factor w.r.t. the microwave mode will be reduced. The refractive index of Pc:PtP is 1.61[28] and that of Ce:YAG is 1.83[29]; their combination, with the latter located inside the former, forms an optical waveguide where reflections off the wedged faces gradually increase the angle of incidence (for pump photons in the waveguide’s core impinging on its cladding) until the critical angle is exceeded and the pump photons escape into the Pc:PtP around it.

Previous arrangements have in contrast used conventional external (“side”) optical pumping where, due to the large mismatch between the refractive indices of Ce:YAG and that of air (= 1), an optical coupling medium (typically oil or glue) is placed between the LC’s outputting face and the receiving face of the gain medium[21, 30]. But such an arrangement is problematic at high optical pump fluences due to photochemical damage/decomposition of either the coupling fluid or the Pc:PtP crystal itself in the presence of oxygen. The charring of either can readily lead to photo-thermal run-away. Here, in contrast, the LC’s output faces are directly in

FIG. 5. (a) 3D-rendered image of the crystal-growth assembly (the upper, empty section of the outer glass vial is not shown). (b) Computer-generated image of the cylindrical Pc:PtP maser crystal (pink) grown around the wedged end of the Ce:YAG LC (lemon yellow) (c) Actual photograph of the red-fluorescing 0.1% Pc:PtP crystal pumped with yellow light from the Ce:YAG (lemon yellow), which itself is pumped by pseudo-white light from a mobile phone’s torch.
contact with the Pc:Ptp crystal, forming a hermetic seal excluding oxygen. The invasive Ce:YAG wedge also functions as a thermal substrate (“heat sink”) for the Pc:Ptp, helping to keep it cool. These two features of invasive optical pumping help to protect the Pc:Ptp from charring. The bright red fluorescence emanating from the Pc:Ptp crystal shown in Fig. 6(c) demonstrates the efficient optical coupling of the LC’s output into the crystal.

C. Maser cavity

The maser cavity used here was an STO ring (Gaskell Quartz Ltd., I.D. = 4.05 mm, outer diameter (O.D.) = 12.0 mm, height = 8.6 mm) housed inside a cylindrical copper enclosure. A support made of cross-linked polystyrene (viz. Polypenco Q200.5 Elder Engineering Ltd., similar to Rexolite) raised the STO ring 3 mm above a copper conducting plane. Fig. 2 shows the cavity setup with the Pc:Ptp crystal loaded inside the STO ring. An inductive loop (coupling coefficient $k = 1$) soldered to an SMA connector was introduced into the copper enclosure to provide an output coupler.

The frequency of the STO-ring-loaded cavity’s $TE_{01δ}$ mode was mechanically tuned (varying the height of the cavity’s internal metal “ceiling” suspended on a screw) to Pc:Ptp’s $|X⟩↔|Z⟩$ transition, i.e. $f_{mode} = f_{XZ} = 1.4495$ GHz. This coupled the microwave photons resident in the $TE_{01δ}$ mode to the spin polarization associated with said transition. The loaded quality factor ($Q_L$) of the $TE_{01δ}$ mode was measured to be 3600 using a vector network analyzer (Agilent 8753C). Due to the high dielectric constant ($ε_r ≈ 312$) of STO at microwave frequencies, the magnetic mode volume of $TE_{01δ}$ was only $V_{mode} ≈ 0.3 \text{ cm}^3$ leading to a high Purcell factor\textsuperscript{[24]} for magnetic-dipole transitions. The magnetic energy density and magnetic field vector of the $TE_{01δ}$ mode were simulated using COMSOL Multiphysics with a 2.5 D axisymmetric model\textsuperscript{[31]}, and are shown in Fig. 6. Magnetic flux is “funneled” through the bore of the STO ring where the Pc:Ptp crystal is located, resulting in a single spin-photon coupling strength of $g_s = γ/2\sqrt{h f_{mode} V_{mode}} = 0.23 \text{ Hz}$, where $γ$ is the electron gyromagnetic ratio, $μ_0$ is the permeability of free-space, and $h$ is Planck’s constant.

The magnetic-dipole moment associated with transitions between the $|X⟩$ and $|Z⟩$ sublevels, as is associated with the $S_Y$ spin-operator, lies along pentacene’s short in-plane molecular axis (i.e. its $y$-axis)\textsuperscript{[22]}. Given (i) the predominately axial polarization of the oscillating magnetic field that the $TE_{01δ}$ mode provides, (ii) the fact that the grown crystal’s predominant cleavage plane contained this axis and (iii) the orientations of the two magnetically inequivalent sites within Ptp’s unit cell that Pc can dope into, it is expected that the average dimensionless magnetic-dipole-transition matrix element (squared)\textsuperscript{[2]} for the stimulated emission (or absorption) between the $|X⟩$ and $|Z⟩$ sublevels will be a reasonably sizeable fraction of unity (depending on the exact crystal orientation).

Determining its value experimentally requires performing “quantitative EPR”, which is complicated by uncertainty in orientation combined with the existence of inhomogeneous broadening, meaning that not all excited pentacene molecules have $|X⟩ ↔ |Z⟩$ transitions (at zero field) in tune with the cavity’s mode, namely $f_{mode} ≠ f_{XZ}$. We doubt that the dilution factor associated with this broadening (for an optically clear Pc:Ptp monocrystal made from pure ingredients) is more than a factor of 10, however.

FIG. 6. 2D axisymmetric simulation of the magnetic energy density (false-color “heat” map) and magnetic field vector (white arrows) of the $TE_{01δ}$ mode of the STO-loaded microwave cavity. The geometries of the STO ring, Pc:Ptp crystal and cross-linked polystyrene support in medial cross-section are highlighted in blue, magenta and red, respectively.

IV. MASER PERFORMANCE

A single pulse (or “flash”) emanating from the xenon lamp inside the head of the IPL source lasts 4 ms and provides a fluence of 2.35 J/cm\textsuperscript{2} (exiting the output face of the fused-silica light guide into air, measured by a Thorlabs ES245C pyroelectric sensor); see Fig. 7. The flash irradiates a rectangular region, 5 mm wide by 34 mm long (equating to an area of $1.7 \text{ cm}^2$) on one of the Ce:YAG LC’s main faces, implying that the LC receives a ~4 J dose of white pump light per flash. Since, the luminescent lifetime of the Ce:YAG is only $\sim 70 \text{ ns}$\textsuperscript{[27]}, the instantaneous-power-versus-time profile of the LC’s yellow output faithfully mimics (i.e. same duration and shape as) that of the primary white pump flash. The energy of this secondary “maser-pump” pulse, entering the Pc:Ptp crystal through the Ce:YAG LC’s output faces, cannot be directly measured. However, adopting the reported power-conversion efficiency of $\sim 17\%$\textsuperscript{[21]} for a similar Ce:YAG LC (with a mirror at one end), we estimate this pump energy to be 680 mJ corresponding to an instantaneous pump power of $\sim 170 \text{ W}$. Upon the Pc:Ptp crystal receiving its pump pulse, a maser burst at 1.4495 GHz, with a peak power of approximately -25 dBm, could...
be detected using a logarithmic detector (Analog Devices AD8318) and was recorded using a digital storage oscilloscope (Tektronix TBS 1102B-EDU, 2 GSa/s sampling-rate, 100 MHz bandwidth); see Fig. 7. The maser burst also has virtually the same duration as that of its optical pump, namely 4 ms (excluding a few μs of start-up delay).

The oscillations observed at the beginning of the maser burst are Rabi oscillations resulting from coupling between the pentacene’s spin ensemble and microwave photons in the TE\(_{01δ}\) mode. Such “Dicke states” have been studied for a similar maser pumped with 5.5 ns pulses of 592-nm light, supplied by an OPO (pumped by a Q-switched Nd:YAG laser) [19]. This is a vastly shorter pump duration than that which is used in the present work (4 ms). Since the measured maser output \(P_{\text{maser}}\) is related to the average number of photons \(\langle \hat{a}^\dagger \hat{a} \rangle\) in the TE\(_{01δ}\) mode according to the expression \(P_{\text{maser}} = h f_{\text{mode}} \langle \hat{a}^\dagger \hat{a} \rangle \kappa_c k/(1 + k)\) [19], where \(k = 1\) is the coupling coefficient of the output port of the cavity, the observed 4-ms maser burst as well as the Rabi oscillations have been simulated (see Fig. 7) by extracting the average photon number \(\langle \hat{a}^\dagger \hat{a} \rangle\) from the following master equations (Eq. 1-6):

\[
\begin{align*}
\frac{d\langle \hat{N}_X \rangle}{dt} &= P_X \eta_{\text{ISC}} \Gamma - k_X \langle \hat{N}_X \rangle - \gamma_X (\langle \hat{N}_X \rangle - \langle \hat{N}_Z \rangle) - \gamma_{XZ} (\langle \hat{N}_X \rangle - \langle \hat{N}_Y \rangle) - ig_a (\langle \hat{S}_+ \hat{a} \rangle - \langle \hat{a}^\dagger \hat{S}_- \rangle) \\
\frac{d\langle \hat{N}_Y \rangle}{dt} &= P_Y \eta_{\text{ISC}} \Gamma - k_Y \langle \hat{N}_Y \rangle - \gamma_Y (\langle \hat{N}_Y \rangle - \langle \hat{N}_Z \rangle) - \gamma_{YZ} (\langle \hat{N}_Y \rangle - \langle \hat{N}_X \rangle) \\
\frac{d\langle \hat{N}_Z \rangle}{dt} &= P_Z \eta_{\text{ISC}} \Gamma - k_Z \langle \hat{N}_Z \rangle - \gamma_Z (\langle \hat{N}_Z \rangle - \langle \hat{N}_X \rangle) - \gamma_{YZ} (\langle \hat{N}_Z \rangle - \langle \hat{N}_Y \rangle) + ig_a (\langle \hat{S}_+ \hat{a} \rangle - \langle \hat{a}^\dagger \hat{S}_- \rangle) \\
\frac{d\langle \hat{S}_+ \hat{a} \rangle}{dt} &= -\kappa_a \langle \hat{S}_+ \hat{a} \rangle - i g_a (\langle \hat{S}_+ \hat{S}_- \rangle + \langle \hat{N}_X \rangle + \langle \hat{a}^\dagger \hat{a} \rangle) \\
\frac{d\langle \hat{S}_+ \hat{S}_- \rangle}{dt} &= -\kappa_a \langle \hat{S}_+ \hat{S}_- \rangle + i g_a (\langle \hat{S}_+ \hat{S}_- \rangle - \langle \hat{a}^\dagger \hat{S}_- \rangle) \\
\frac{d\langle \hat{a}^\dagger \hat{a} \rangle}{dt} &= -\kappa_a \langle \hat{a}^\dagger \hat{a} \rangle - \bar{n} + i g_a (\langle \hat{S}_+ \hat{a} \rangle - \langle \hat{a}^\dagger \hat{S}_- \rangle)
\end{align*}
\]

Here, the population of pentacene molecules in a state or sublevel \(L \in \{ |X\rangle, |Y\rangle, |Z\rangle \} \) is expressed as the expectation value of the number operator \(\hat{N}_L\), respectively. \(\hat{S}_+, \hat{S}_-\) and \(\hat{a}^\dagger \hat{a}\) are, respectively, the operators of spin-photon coherence, spin-spin coherence and the photon number in the TE\(_{01δ}\) mode. \(\hat{S}_Z = \hat{N}_X - \hat{N}_Z\) is the spin polarization between the \(|X\rangle\) and \(|Z\rangle\) triplet sublevels. The optical pump rate is evaluated as \(\Gamma = \eta_{\text{opt}} P_{\text{pump}}/h f_{\text{pump}}\), where \(\eta_{\text{opt}}\) is a dimensionless parameter adjusting the overall efficiency of the pumping process (it has no relation to the previously mentioned maser "co-operativity"). We found the best-fit value of the efficiency \(\eta_{\text{opt}}\) is about 5.4%. The inefficiency can be attributed to (i) the inhomogeneous broadening of pentacene (\(\sim 4\) MHz) such that only about 10% of the pentacene molecules with the \(|X\rangle \leftrightarrow |Z\rangle\) transition match the cavity’s linewidth (\(\sim 400\) kHz), and (ii) the misalignment between the mode’s magnetic field and pentacene’s magnetic-dipole moment lying along the short in-plane molecular axis. \(P_{\text{pump}}\) is the instantaneous power of the pump “beam” coming from the Ce:YAG luminescent concentrator; \(f_{\text{pump}}\) is the optical frequency of the LC’s peak emission at 528 nm; and \(\eta_{\text{ISC}}\) is the ISC yield (\(\sim 62.5%\)) that can be evaluated according to \(\eta_{\text{ISC}} = k_{\text{ISC}}/(k_{\text{ISC}} + k_{\text{sp}})\). The rate of the spontaneous emission \(k_{\text{sp}} = 4.2 \times 10^7\) s\(^{-1}\) and the ISC rate \(k_{\text{ISC}} = 6.9 \times 10^7\) s\(^{-1}\) [25]. \(P_X = 0.76\), \(P_Y = 0.16\) and \(P_Z = 0.08\) are the normalized \((P_X + P_Y + P_Z = 1)\) spin-selective population rates for transfers of population mediated by inter-system crossing into \(T_1\)’s \(|X\rangle, |Y\rangle\) and \(|Z\rangle\) sublevels. Because internal conversion from \(T_2\) to \(T_1\) (in Fig. 1) is both extremely fast and spin-polarization...
preserving, one can regard the ISC process as moving population directly from $S_1$ into $T_1$'s three sublevels.

Our best-fitted triplet decay rates ($k_i$) and the spin-lattice relaxation rates ($\gamma_{ij}$) are shown in Table. 1. We note that the values obtained for $k_X$, $k_Y$ and $\gamma_{YZ}$ differ slightly from those reported in our previous study[20]. We suspect that the discrepancies stem from the different light sources used for pumping the Pc:Ptp crystal. In ref. [20], an optical parametric oscillator (OPO), providing a monochromatic output at 590 nm, was used. Light at this wavelength can only be absorbed via pentacene's $S_0 \rightarrow S_1$ transition. In contrast, the Ce:YAG LC's output spans a relatively broad range of wavelengths as shown in Fig. 4 which may further induce the optical excitation of pentacene molecules in $T_1$ to higher triplets states (e.g. $T_1 \rightarrow T_3$[35][36]), potentially altering the triplet spin dynamics. $\kappa = 2\pi f_{XZ}/Q_L = 2.5$ MHz is the cavity decay rate. $\kappa_S = 1.1$ MHz is the spin-dephasing rate of the pentacene’s triplets which is larger than the value measured by zero-field pulsed EPR free induction decay (FID) in a separate study (0.7 MHz)[32]. The difference may arise from a concentration effect[35]; our Pc:Ptp crystal had a doping concentration of 0.1% whereas that may arise from a concentration effect[35]: our Pc:Ptp (FID) in a separate study (0.7 MHz)[32]. The difference between the mean number of thermal photons in the TE$_{01\delta}$ mode and the frequency of the maser transition $|X\rangle \leftrightarrow |Z\rangle$ and shifts in both the frequency of the maser transition $|X\rangle \leftrightarrow |Z\rangle$ and the frequency of the maser cavity's TE$_{01\delta}$ mode (upon the crystal transferring its acquired warmth to the STO surrounding it). Using Figure 4 of ref. [39], the temperature dependence of the former can be estimated to be -80 kHz/K. Considering an extreme case that the optical pump energy is completely transferred to the dielectric ring containing $2.3 \times 10^{-2}$ mol of STO whose heat capacity is $\sim 100$ J K$^{-1}$ mol$^{-1}$[40], the maximum temperature rise of the STO should be $\sim 0.3$ K. Using the known Curie-Weiss temperature dependence of STO’s dielectric constant [41], the temperature dependence of the latter is estimated to be around +2.6 MHz/K. These changes could certainly degrade the maser’s output power as seen in Fig. 7. The observed thermal issue implies that, as with many types of CW lasers, active cooling of the gain medium will be required for sustained operation and that, if the resonator is adjusted to match the frequency of the maser transition when the crystal is continuously pumped (and thus warm), there could be an initial delay in the onset of masing as the crystal warms up.

The previous study[13] showed that a certain figure of merit, $\kappa$, with an expression of

$$
\kappa = P_x [1 + (k_Y + k_Z + k_{YZ}/\gamma_{XY})/k_X] - (P_x/\gamma_{XY}) (k_Y + \gamma_{YZ}[1 + (k_Y + k_Z)/k_X]) + (k_Z/k_X)(\gamma_{YZ}/\gamma_{XY}) - 1
$$

must exceed zero for continuous masing to be possible. Using the spin dynamics extracted from the simulation, we evaluated that $\kappa = 0.2$, which indicates that our setup in this work is feasible for operating a pentacene maser in a CW mode at room-temperature.

V. CONCLUSION AND OUTLOOK

In summary, pumped by a Ce:YAG LC with an output power of 170 W, a room-temperature quasi-CW pentacene maser has been successfully achieved. It can operate continuously for 4 ms with a peak power of -25 dBm. Although this is preliminary work for realizing a CW pentacene maser, the results have solved a long-standing mystery about whether the pentacene maser can work in a CW mode or not. We found that it is perfectly possible for the pentacene maser to run in a CW mode provided the heat generated by optical pumping of the gain medium can be removed effectively. Flowing argon gas around the pentacene gain medium might be a solution. Similar to LC pumped CW lasers[30][42], a high power light-emitting diode could be used, in lieu of a flash lamp, to pump the Ce:YAG LC (combined with invasive optical pumping) and power the pentacene maser. As an efficient pump source, LCs offer the advantages of low cost, low maintenance and simple fabrication, which would support the future development of cheaper, high-power solid state lasers/masers.

| $k_X$ | $k_Y$ | $k_Z$ | $\gamma_{XY}$ | $\gamma_{YZ}$ | $\gamma_{XZ}$ |
|-------|-------|-------|--------------|--------------|--------------|
| 2.8±0.5 | 0.6±0.2 | 0.2±0.09 | 1.1±0.2 | 2.2±0.2 | 0.4±0.2 |
| 2.2 | 1.4 | 0.2 | 1.1 | 2.8 | 0.4 |

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