Toward maser action at room temperature by triplet-radical interaction and its application to microwave technology

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The interaction between photoinduced triplets and stable radicals, in liquid solutions at room temperature, is utilized to control the macroscopic permeability of these systems. Based on a numerical-theoretical treatment, which describes this photoprocess, the changes in the permeability can be optimized by choosing the appropriate chemical system. Presently, we can demonstrate how these light-driven changes result in noticeable changes in the reflection coefficient (amplitude and phase) of a microwave cavity containing the chemical system. This effect can lead the way to ultra low noise microwave amplifiers and low-loss microwave phase shifters, operating at room temperature with very low spin temperature, *e.g.*, $T_s < 16$ K.

Introduction

Controlling the magnetic permeability in paramagnetic materials is recognized as an important feature in microwave technology.[1,2] The general concept is to exploit changes in the electron spin population of the magnetic Zeeman levels, thus allowing to amplify the electromagnetic radiation in the bulk material. These early studies resulted in the three-level solid-state maser (microwave amplification by stimulated emission of radiation) amplifier, based upon the paramagnetic properties of the electron.[3] The main advantage of using the maser is typified by its extremely low-noise figure as compared to conventional microwave amplifiers, *e.g.*, vacuum tubes and GaAs field effect transistors (FETs).

To achieve amplification in a paramagnetic-based maser, one must achieve inverted spin population, which corresponds to a negative spin temperature. In conventional masers, this is carried out by microwave pumping at very low temperatures (T < 2 K). The restriction of low temperatures, which precluded the wide use of masers, can be accounted for by two reasons. First, by microwave pumping, high population inversion can be achieved only if $k_BT \ll h\nu$. Secondly, the active materials in the microwave pumped masers,[4] exhibit a very steep dependence of the spin-lattice relaxation (SLR) time upon temperature. Thus, at high temperatures, the fast relaxation cannot allow for efficient pumping of the magnetic levels. Pumping the levels by optical excitation, can overcome the first difficulty and achieve the condition $k_BT \ll h\nu$ even at room temperature.[4-7] Nevertheless, the second constraint of short SLR time, still limits the maximum temperature of operation to 10 K.

Electron spin polarization and permeability

The population difference (ΔN) between the spin levels is directly related to the macroscopic magnetic permeability of the active material, $\mu = 1 + 4\pi\kappa$, where the volume magnetic susceptibility, $\kappa = \kappa' - i\kappa''$, is expressed by:[8]

$$\kappa''(\nu - \nu_0) = \Delta N/8 \cdot \gamma^2 \cdot (1.75) \cdot f''(\nu - \nu_0), \quad (1)$$

γ is the electron gyromagnetic ratio (1.76×10^7 G^{-1}s^{-1}) and $f''(\nu - \nu_0)$ is the normalized absorption/emission line shape function (usually a Lorentzian)[9] with a maximum at ν_0. The real part of the bulk (volume) magnetic susceptibility, κ', which is related to the signal phase can be obtained by replacing the line shape function $f''(\nu - \nu_0)$ with the function $f'(\nu - \nu_0)$.[8] Thus, Eq. (1) shows that the bulk permeability can be controlled through the radical line width $\Delta\nu$ and the population difference, ΔN, which is directly related to electron spin polarization (ESP). Changing ΔN from thermal to non-thermal equilibrium can be achieved by a variety of photochemical and photophysical processes.[10,11] The classical spin polarization mechanisms such as triplet mechanism (TM)[12] or radical-pair mechanism (RPM)[13] are not suitable for maser operation at room temperature due to the short life time of the polarization, inhomogeneous line broadening, and in many cases the irreversibility of the processes by photo degradation. However, a different mechanism, introduced in the last decade, involves the interaction of triplets and stable radicals in liquid solution, which may be more useful for applied purposes. The ESP generated by this photoprocess is based on two fundamental mechanisms, namely electron spin polarization transfer (ESPT) and radical-triplet-pair mechanism (RTPM).[11,14-16] These intermolecular processes can generate high spin polarization, which leads to high magnetization that is maintained for a relatively long periods of time, even at room temperature.[17] Moreover, changing the ingredients of the chemical system. i.e., solvent viscosity, zero-field splitting (ZFS) parameter, radical size and it's EPR line width can control the parameters, which determine the temporal behavior of the magnetization.

To optimize the conditions of generating high and long-lived polarized magnetization, one must have detailed knowledge of the mechanisms involved. This has been achieved by developing a new numerical-theoretical approach for calculating the radical polarization and its magnetization, which is focused on the following points:[18] (1) Providing a general
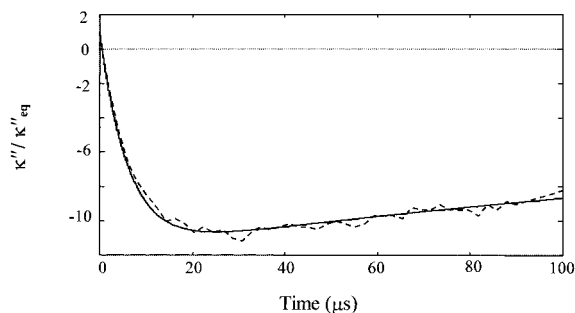
Fig. 1. Experimental temporal behavior (dashed line) of the magnetic susceptibility normalized to the thermal susceptibility, κ''/κ''_{eq}, and the corresponding calculated curve (solid line) resulting from the numerical solution.[18] The measurement was carried out with a BDPA radical and tetraphenylporphyrin triplet. The figure shows the relatively long lifetime of the phenomenon (several hundreds of μs at room temperature) and the high ESP achieved (more than 10 times the thermal polarization).
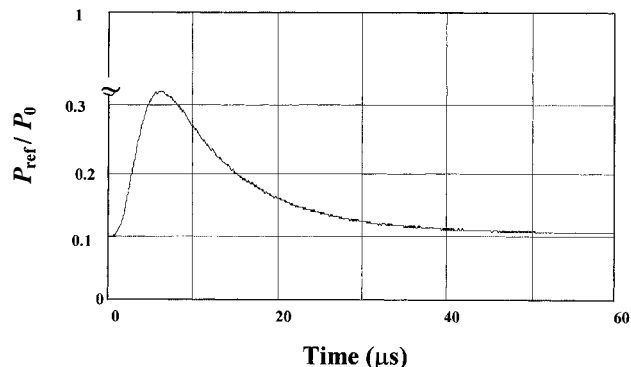

Fig. 2. Time dependence of the reflection coefficient, measured for the system of trityl radical and etioporphyrin triplet. To maximize the degree of polarization (ESP) and to optimize the changes in the cavity's reflection coefficient, a specially designed dielectric cavity was employed to achieve high values of Q_L and η (see Eq. 3).

treatment taking into account low and high solvent viscosities, in which the radical polarization is generated by the encounters of polarized or non-polarized triplets with polarized or non-polarized radicals. The case of having a polarized radical, prior to the encounter, is of importance. In some recent experiments, the radical exhibited a very long spin-lattice relaxation (SLR) time ($T_1^R > 100\,\mu$s). In this case, the encounters of triplets and polarized radicals should affect both the ESPT and RTPM processes. For example, a possibility not discussed in the past is the interaction of a polarized radical and a non-polarized triplet, where the polarization transfer is likely to occur preferentially from the radical to the triplet. Moreover, the involvement of polarized radicals may affect the efficiency of RTPM; (2) When the encounter time is comparable to the triplet's SLR time, an additional factor is considered. It is related to the spin relaxation of the triplets and radicals, which occurs during the encounter and results in a decrease of the radical polarization after separation; (3) As shown qualitatively,[17] RTPM polarization is generated even when the triplet quenching by the radical is not complete. The efficiency of the triplet quenching is related to that of the excited doublet depletion and evidently, will affect the overall radical magnetization. In other words, efficient triplet quenching may lead to high radical polarization in a single encounter, but at the same time it will reduce very fast the triplet population and decrease the overall radical magnetization. Thus, the influence of triplet quenching efficiency on the resulting radical polarization and magnetization is also considered; and (4) In addition to the calculation of the radical polarization, a detailed kinetic model, which predicts the time evolution of the radical magnetization, provides the final step in the theoretical treatments.

An example for the calculated results of the magnetization time dependence is given in Fig. 1. These theoretical predictions enabled us to choose the best set of parameters, such as the triplet, radical and solvent viscosity, in order to optimize the radical's polarization and magnetization.

The application of ESP to microwave devices

Achieving high polarization for a long period of time, allowed us to demonstrate a preliminary device operating at room temperature, based on a chemical system, which upon photoexcitation exhibits an ESP effect.[19] With this prototype we could change the amplitude and phase of the loaded cavity's reflection coefficient (P_{ref}) due to photoinduced permeability changes of the chemical system (Fig. 2). Currently, we have achieved a change of –25% in the reflected wave, relative to the impinging wave.

The experimental results of Fig. 2 can be discussed through the relation between reflection coefficient, P_{ref}, and the permeability, μ. For a nearly critically coupled cavity, and within the first-order approximation of small changes in the reflected power, ΔP_{ref}, one obtains:[20]

$$\frac{\Delta P_{ref}}{P_0} = \pm i 0.193 \cdot 4\pi \cdot \kappa \eta Q_c = \pm 0.193 \cdot 4\pi \cdot \eta Q_c \left| \kappa \right| e^{i\varphi}. \tag{2}$$

ΔP_{ref} is a complex number whose phase is related to the cavity's coupling properties and the radical's ESP mode (absorption or emission), P_0 is the incident microwave power on the cavity, η is the filling factor of the illuminated sample,[20] $\varphi = \arctan\left(\kappa'/\kappa''\right)$, and Q_c is the quality factor of the cavity with the sample. Inserting all the system parameters into Eq. (2) results in the calculated change of $\Delta P_{ref}/P_0 = 0.3$ for the cavity we employed, at room temperature. This value fits well with the experimental findings shown in Fig. 2, which shows a change of –0.25 in ΔP_{ref} of the cavity. In addition to the amplitude change of P_{ref}, a phase change of –30° was measured.

For maser action, the threshold value requires that the amplification due to κ'' should be larger than the dielectric losses, i.e.,[8]

$$\kappa'' > (4\pi \cdot \eta \cdot Q_L)^{-1}, \tag{3}$$

where $1/Q_L = 1/Q_c + 1/Q_{ex}$ and Q_{ex} corresponds to additional losses of power delivered to the external load.[8] Further improvements of the cavity's filling factor and of the chemical system, may close the gap between the current performance and the required one for achieving this threshold (a factor of 4).

The noise performance of the maser as an amplifier is determined mainly by the maser's spin temperature, which is directly related to the degree of population inversion (ESP magnitude). We have achieved a spin temperature smaller than 16 K, at room temperature. Therefore, realization of such a maser, can lead to new types of microwave amplifiers, operating at room temperature and still maintaining a low noise figure. Such amplifiers can be utilized, for example, in satellite communication systems or cellular base stations for increasing the range of communication channel.[19]

To summarize, this work demonstrates the application aspects of ESP, generated by a photophysical process at room temperature. Further improvements of the cavity's structure and optimization of the chemical systems, to provide increased ESP, should pave the way to achieve the threshold for maser action.

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