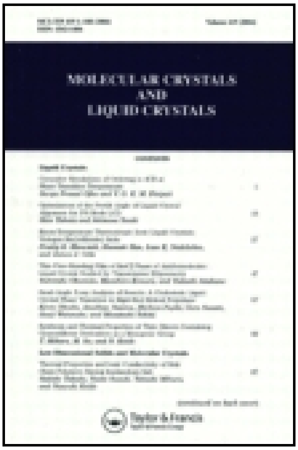

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Hole-Burning Studies on Triplet-Triplet Fluorescence Excitation Spectrum of 2-Naphthylphenylcarbene

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HOLE-BURNING STUDIES ON TRIPLET-TRIPLET FLUORESCENCE EXCITATION SPECTRUM OF 2-NAPHTHYLPHENYLCARBENE

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Abstract Spectral holes were burned on the triplet-triplet 0-0 fluorescence excitation lines of main conformers of 2-naphthylphenylcarbene in n-hexane and n-heptane at 1.8 K. The central holes, at a frequency of laser burning light have usually several accompanying satellite holes in a range of 1.5 GHz around and deep holes on the low energy side, 14.5 - 16.5 GHz away. Such a pattern of holes reflects the zero field splitting of the ground T_0 and first excited T_1 triplet states and the fact that an energy relaxation by the intersystem crossing channel is highly selective.

INTRODUCTION

The zero field splitting (ZFS) parameters of triplet states, which provide information about the distribution of unpaired electrons, are usually obtained by the EPR technique. This technique is however difficult or impossible to apply to very short-lived triplet states. It is the case of 2-Naphthylphenylcarbene (2-NPC) which, like parent methylene, is a carbene with a triplet ground state, T_0. The fluorescence emission of 2-NPC corresponds to a $T_1 \rightarrow T_0$ transition and thus the lifetime of the excited triplet state

T_1 is quite short, only a few nanoseconds [1]. Depending on the mutual orientation of the naphthyl and phenyl rings, 2-NPC can exist in different conformations - the energetically most favourable forms are the two pseudo-planar conformers of 2-NPC, pseudo-E/trans and pseudo-Z/cis.[2]

The triplet-triplet fluorescence and fluorescence excitation spectra of 2-NPC in n-hexane and n-heptane Shpol'skii matrices are composed of sharp bands, which were attributed to different conformers of 2-NPC [3,1]. A coincidence of the profiles of corresponding fluorescence and fluorescence excitation 0-0 lines clearly indicates that they are zero-phonon lines, which provides the background for hole-burning investigations.

Recently [4], we have shown that hole-burning is possible on the fluorescence excitation spectrum of the two main conformers of 2-NPC in n-hexane at 1.8 K. For the first time this technique provides an alternative, direct and precise method to obtain the ZFS parameters of the excited T_1 and ground T_0 triplet states. In the present contribution we extend the hole-burning studies to 2-NPC in an n-heptane matrix and compare all of the hole-burning spectra of 2-NPC which we have observed.

RESULTS AND DISCUSSION

Typical hole-burning spectra are collected in Fig.1. It was possible to burn holes on 3 fluorescence excitation lines of 2-NPC dispersed in n-hexane, at 588.7 (a), 598.2 (b) and 600.1 nm (c) and on 2 lines of 2-NPC in n-heptane, at 582 (d) and 600.5 nm (e). An effort to burn holes on the 582.6 nm fluorescence line of 2-NPC in n-hexane and on the 589.5 nm fluorescence line of 2-NPC in n-heptane [1] was unsuccessful, probably because of unfavorable Debye-Waller factors. The experimental conditions which produce the best signal to noise ratio were very much different for the high (cases a and d) and for the low (cases b, c and e) energy lines. In the former cases, we used a burning intensity of laser light (with 1 MHz frequency resolution) of about 1.5 mW/cm^2 and a precursor concentration of 10^{-3} - $5 \cdot 10^{-4}$ M, whereas in the latter these were about 0.1 mW/cm^2 and $5 \cdot 10^{-3}$ M. The reading intensity was weaker by 10 - 100 times than the light intensity used for burning of holes. It was necessary to use very low burning intensity for the low energy fluorescence excitation lines because of the very high burning efficiency. This is probably connected to the light-induced transformation from the pseudo-Z/cis (with a fluorescence origin at 600.5 nm) to the pseudo-E/trans 2-NPC (with a fluorescence origin at 589.5 nm), when the sample was illuminated by a 337 nm N_2 laser light. This process was experimentally observed in n-heptane matrix but not in n-hexane [1,3]. This interpretation is in agreement with the fact that a burning efficiency

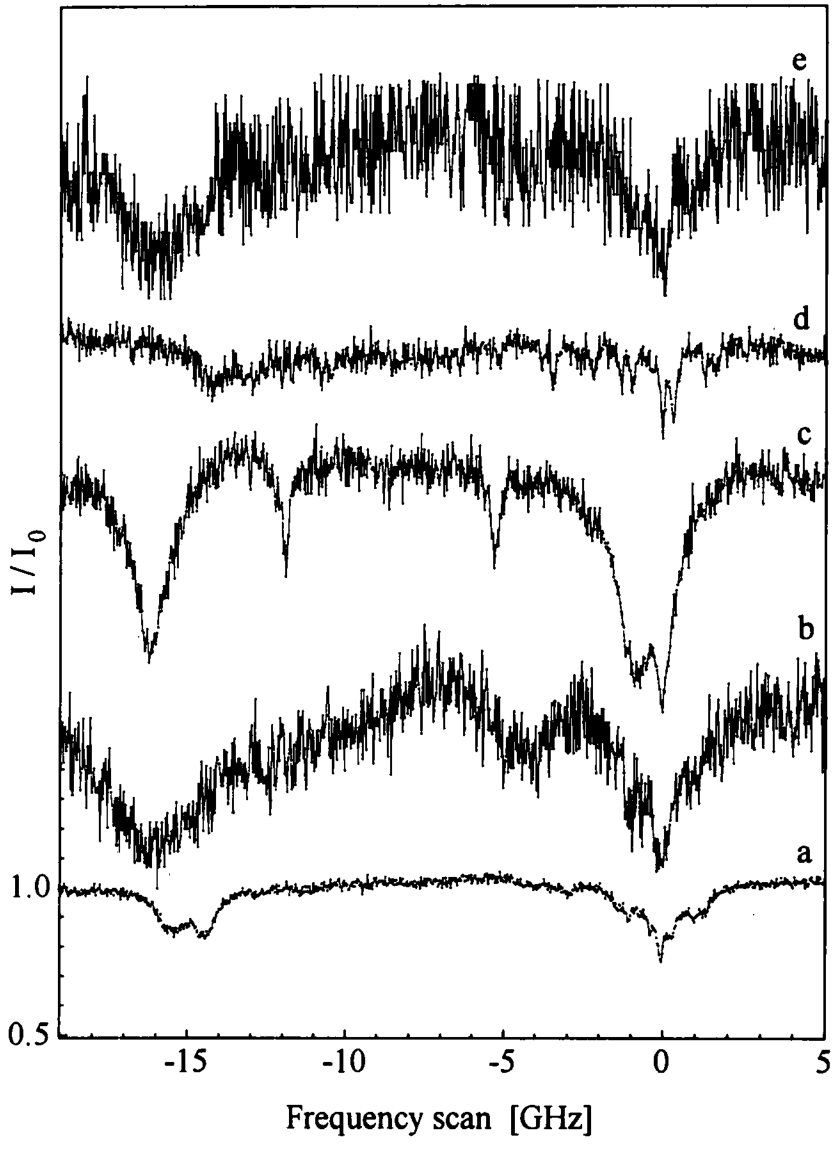

FIGURE 1 Typical holes burned within the inhomogeneous profiles of 0-0 triplet-triplet fluorescence excitation lines of 2-NPC in n-hexane (a, b, c) and n-heptane (d, e) at 1.8 K. (a) - 588.7 nm; (b) - 598.2 nm; (c) - 600.1 nm; (d) - 582.0 nm; (e) - 600.5 nm line. To improve the signal to background ratio, the fluorescence intensity was detected at the main vibronic line, 1380 cm^{-1} away from the respective 0-0 fluorescence origin [1]. The spectral positions of holes are given in respect to the frequency of burning light.

of the conformer having the fluorescence origin at 600 nm is higher in n-heptane than in n-hexane.

There are several characteristic features common to all of the burned holes. The central holes, at the frequency of the burning light, are surrounded by some satellite holes in a range of 1.5 GHz. Other deep satellite holes are located on the low energy (red) side, about 15 GHz away. On the high energy (blue) side of the central holes (not shown in Fig.1) we were not able to detect any additional holes (The only exception is the case of the 600.1 nm line in n-hexane, where a very weak satellite hole, barely distinguished from noise, was observed some 15.5 GHz to the high energy side of the central hole). We estimate that the area of possible blue satellite holes are at most 10% of the area of the central hole.

The presence of satellite holes is connected with the ZFS of the ground T_0 and excited T_1 triplet states. The hole-burning laser light excites the 2-NPC molecules whose $T_0 \rightarrow T_1$ transition energies are in resonance with the laser frequency. The excited 2-NPC may relax by radiative and nonradiative channels. The latter path results in a transfer of energy to the surrounding matrix and the 2-NPC/matrix system may jump from a local energy minimum to some other leaving a spectral hole at the previous position of the zero-phonon excitation line.

The lack of holes on the high energy side indicates that the group of carbenes which absorb light when they are in the lowest energy spin sublevel of T_0 are the only which effectively contribute to the hole-burning spectrum [4]. In the T_0 state of 2-NPC, as in the case of methylene, the two unpaired electrons are approximately localized on the central C atom and occupy the $(p_x)^1 (sp_y)^1$ orbital configuration. Thus, the ZFS parameter D_0, which is inversely proportional to the third power of the separation between unpaired electrons, has a large value. The lowest energy spin sublevel is T_{0z} and this sublevel is strongly favored compared to the other two during the intersystem crossing relaxation process $S_1 \rightsquigarrow T_0$ as it was established by the electron spin echo experiments for the related carbene, diphenylmethylene [5]. This implies, that during the nonradiative relaxation via the intersystem crossing channel, $T_1 \rightsquigarrow S_4 \rightsquigarrow S_1 \rightsquigarrow T_0$, the 2-NPC molecules are pumped by the burning light to the T_{0z} sublevel and remain there during the characteristic spin-lattice relaxation time, which is rather long at 1.8 K. The only group of carbenes which can continuously interact with the burning light (and thus be burned) are those which are in the T_{0z} sublevel. [4]

In the T_1 state, one of the unpaired electrons is promoted to a (π^*) orbital delocalized on the naphthalene ring and the π spin density on the carbenic center decreases. Consequently, the average separation between unpaired electrons increases and the ZFS parameter D_1 of the T_1 state is much smaller than that in the ground state. [1]

The electronic distribution in the T_0 and T_1 states are very different and therefore the directions of the spin axes (and even the ordering of spin sublevels) may be quite different in both states. Electronic transitions are then possible from every spin sublevel of T_0 to every spin sublevel of T_1.

From the above considerations we conclude that hole-burning may be efficient for three groups of molecules, those for which the burning light is resonant with $T_{0z} \rightarrow T_{1x'}$, $T_{0z} \rightarrow T_{1y'}$ and $T_{0z} \rightarrow T_{1z'}$ transitions. Now, the central hole, at the frequency of burning light, should be symmetrically surrounded by 3 satellite holes on the low energy side and 3 holes on the high energy side, with energy separations related to D_1 and E_1, the ZFS parameters of T_1. Two other deep holes, each composed of 7 component holes, are expected on the low energy side of the central hole, $(D_0 - E_0)$ and $(D_0 + E_0)$ away.

Such a scheme of expected holes fits very well with the real hole-burning spectra detected on the 588.7 nm fluorescence excitation line of 2-NPC in n-hexane (Fig. 1a) where the ZFS parameters are: $D_0 = (0.47 \pm 0.02)$ cm^{-1}, $E_0 = (0.017 \pm 0.003)$ cm^{-1}, $D_1 = (0.038 \pm 0.003)$ cm^{-1} and $E_1 = (0.005 \pm 0.001)$ cm^{-1}.[4] It is difficult at the moment to propose an adequate model to explain in detail the pattern of holes burned on the other fluorescence excitation lines (Fig. 1b-e). It seems reasonable to expect that the energy separation between the central and deep holes, burned on the low energy side of spectra, provide a crude estimation of the D_0 parameters. An inspection of Fig. 1 shows that this separation is larger for the 2-NPC conformers with 0-0 excitation bands at 600.1 and 598.2 nm in n-hexane (and at 600.5 nm in n-heptane) than the conformers with 0-0 excitation bands at 588.7 nm in n-hexane (and at 582.0 nm in n-heptane). Using the theoretical arguments of ref. [2] and [6] indicating that the D_0 parameter is smaller for the pseudo-E/trans than for the pseudo-Z/cis conformer of 2-NPC we may conclude that the 0-0 fluorescence excitation lines at 582.0 and 588.7 nm (cases d and a of Fig. 1) may be assigned to the former conformer whereas the lines at 598.2, 600.1 and 600.5 nm (cases b, c and e of Fig. 1) to the latter one. This last conclusion is consistent with the results of our previous work[1].

The very great depth of burned holes (up to 80%) as well as the presence of holes located between the central holes and the side holes for the 598.2, 600.1 and 600.5 nm fluorescence excitation lines are puzzling. It may be misleading to relate these observations to the ZFS parameters of the ground and excited triplet states but a precise (and independent) estimation of the ground state ZFS separations for every conformer seems to be crucial. Furthermore, the origin of the burned holes within the fluorescence excitation line of pseudo-Z/cis 2-NPC may be of a photochemical nature. This work is in progress and an explanation of the above features will be the aim of forthcoming investigations.

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