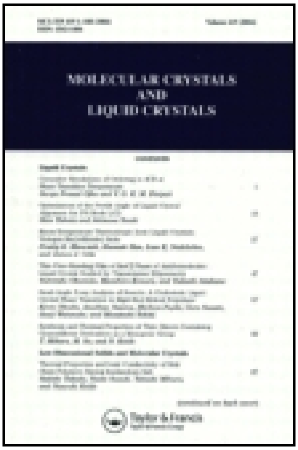

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ZERO-FIELD SPLITTING OF THE T_0 AND T_1 STATES OF 2-NAPHTHYLPHENYLCARBENE FROM HOLE BURNING STUDIES OF TRIPLET-TRIPLET TRANSITION

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Abstract Spectral holes have been burned on the 0,0 fluorescence excitation ($T_0 \rightarrow T_1$) line of 2-naphthylphenylcarbene in n-hexane at 1.8 K. A complicated spectrum of holes reflects zero-field splitting of both the triplet states, T_0 and T_1, and provides a way to estimate their splitting parameters D_0, E_0, D_1 and E_1. Comparison of the real hole burning spectrum with the simulated one suggests possibility of a distribution of burning yields and/or a distribution of homogeneous linewidths of 2-naphthylphenylcarbene molecules located in different sites of a Shpol'skii matrix.

INTRODUCTION

Molecules of 2-naphthylphenylcarbenes (2-NPC) are created by photolysis of the appropriate diazo precursors and have two non-bonding electrons which result in a triplet ground state (T_0).[1] This compound is a short-lived reaction intermediate in the gas or liquid phase but it is relatively stable in a cryogenic matrices, where friction greatly restricts molecular motion and effectively eliminates intramolecular reactions.

The triplet-triplet fluorescence ($T_1 \rightarrow T_0$) and fluorescence excitation ($T_0 \rightarrow T_1$) spectra of 2-NPC in Shpol'skii matrix of n-hexane at 1.8 K are composed of zero-phonon lines [2] which provided background for the first hole burning experiments on triplet-triplet transition [3,4]. In the present contribution we compare the hole burning spectra, real and simulated, of the pseudo-E/trans conformer of 2-NPC. This conformer is photostable (fluorescence intensity of this conformer do not change under illumination) and its 0,0 fluorescence line has maximum at 588.7 nm. [2]

RESULTS AND DISCUSSION

Typical spectrum of holes, burned within the inhomogeneous profile of 0,0 fluorescence excitation line (between 588.6 and 588.8 nm) of the pseudo-E/trans conformer of 2-NPC in n-hexane at 1.8 K is shown in Fig. 1. It composes of several sharp holes located symmetrically around the central hole, which has been burned at the frequency of applied laser light (0 GHz in Fig. 1), and of two broad deep holes, located at low energy side of the central hole. We were not able to detect any holes on the high energy side of the central hole.

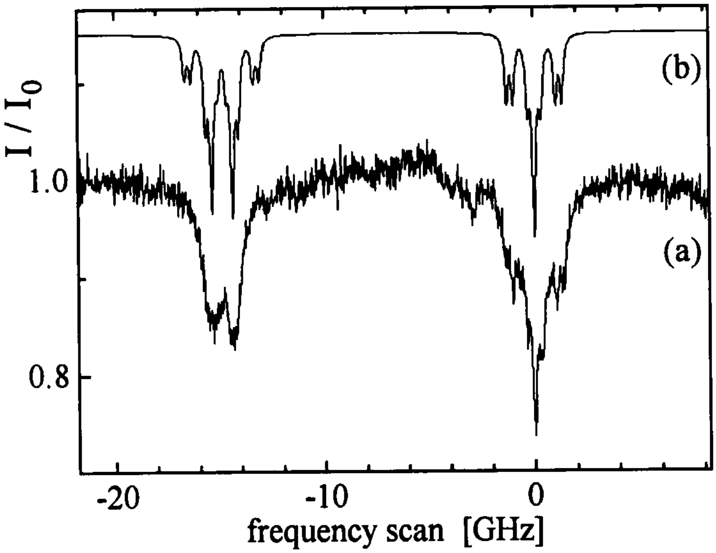

FIGURE 1 Experimental (a) and simulated (b) spectrum of burned holes of pseudo-E/trans conformer of 2-NPC in n-hexane at 1.8 K. Details in the text.

The above spectrum can be explained [3,4] when taking into account that each active in the electronic transition triplet state, T_0 and T_1, has three zero-field splitting (ZFS) spin sublevels. Furthermore [3]:

- the ZFS parameters D_0 and E_0 of the ground T_0 state are considerably higher than the D_1 and E_1 parameters of the excited T_1 state (this difference reflects the fact that in the T_0 state the two unpaired electrons are approximately localized on the central carbonic atom whereas in the T_1 state one of the unpaired electrons is delocalized onto the naphthalene ring);
- the only group of 2-NPC which can effectively contribute to the bole-burning spectrum is that in which carbenes are in the lowest energy spin sublevel of the ground state, T_{0z}, when they are in resonance with a burning laser light;
- the ZFS principal spin axes are different in the T_0 and T_1 states (these axes follow the redistribution of electronic density) and the electronic transitions from every spin sublevel of the ground state (T_{0x}, T_{0y} and T_{0z}) to every spin sublevel of the excited state ($T_{1x'}$, $T_{1y'}$ and $T_{1z'}$) are allowed.

The above, two last conditions require that hole burning may be efficient for three groups of carbenes, those for which the burning light is in resonance with the $T_{0z} \rightarrow T_{1x'}$, $T_{0z} \rightarrow T_{1y'}$ and $T_{0z} \rightarrow T_{1z'}$ transitions.

Now, the central hole, at the frequency of laser light, should be symmetrically surrounded by 3 satellite holes on the low energy side and 3 satellite holes on the high energy side, located $2 \cdot E_1$, $(D_1\text{-}E_1)$ and (D_1+E_1) away. Spectral positions of these holes provide unique possibility to estimate the ZFS parameters of the excited, short-lived T_1, state. Two other sets of holes, each composed of 7 holes and closely resembling the structure of holes around the central hole, are expected on the low energy side of the central hole, $(D_0\text{-}E_0)$ and (D_0+E_0) away. [3] Spectral positions of these holes provide information about the ZFS parameters of the ground, T_0, state and can be also obtained by EPR technique.

The expected, simulated spectrum of holes is shown at the top of Fig. 1, above the experimental spectrum. This simulated spectrum has been obtained using an assumption that each satellite hole has a lorentzian shape with fwhm = 0.2 GHz and that: $D_1 = 1.15$ GHz, $E_1 = 0.15$ GHz, $D_0 = 15.0$ GHz and $E_0 = 0.5$ GHz. Populations of the spin sublevels, T_{0x}, T_{0y} and T_{0z}, which have been used in calculations are taken according to the Boltzman's equilibrium at 1.8 K.

Inspection of both the spectra presented in Fig. 1 indicates that an energetic position of burned holes are predicted pretty well but a shape of real spectrum is clearly more complex than a simulated one. In excess to a contribution of sharp holes (with fwhm = 0.2 GHz) a real spectrum has a contribution of some broader holes as well. Such a behavior suggests possibility of a distribution of the hole burning yields (η) and/or a distribution of the homogeneous linewidths (γ), which should be measured on the experimental time scale. N-hexane Shpol'skii matrix has a polycrystalline structure and molecules of 2-NPC may occupy many different sites in this matrix, leading to distribution of their physical quantities. It is difficult to elucidate at present which of the mentioned distributions is more crucial. Dependence of the hole-width v. fluency is lacking, what unables us to conclude about a distribution of η. A distribution of γ can be precisely obtained from experiments on single molecules but unfortunately, our effort to detect a single 2-NPC was unsuccessful, probably because of a low fluorescence quantum yield of this compound. It is also possible that some smoothing of the substructures in the hole profiles originates from a distribution of ZFS parameters of the T_0 and T_1 states of 2-NPC located in slightly different sites of n-hexane matrix.

The work on hole burning spectrum of 2-NPC in Shpol'skii matrix of n-hexane (and n-heptane) at 1.8 K is still in progress and the forthcoming investigations should bring a deeper inside into precise determination of the ZFS parameters of the both involved triplet states as well as to explain the role of a matrix.

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