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A Hole-Burning Study of the Zero-Field Splitting of the Triplet Ground and Excited States of 2,2-Dinaphthylcarbene in *n*-Heptane and *n*-Hexane at 1.7 K

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Spectral holes were burned within the inhomogeneous 0,0 fluorescence excitation lines of the $T_0 \rightarrow T_1$ transition of 2,2-dinaphthylcarbene (2,2-DNC) in *n*-heptane at 1.7 K. The spectrum of holes, attributed to the Z/cis conformer of 2,2-DNC, was interpreted with a model taking into account the zero-field splitting (zfs) of both triplet states contributing to the transition, enforced C_{2v} symmetry, and the dominance of internal conversion in the relaxation of the excited T_1 state. Under enforced high symmetry, the number of possible electronic transitions between different spin sublevels of the ground T_0 and excited T_1 states is reduced and the analysis of spectral position of holes can only provide the differences between the zfs parameters: $D_0 - D_1 = 0.558 \pm 0.001$ cm^{-1} and $E_0 - E_1 = 0.0183 \pm 0.001$ cm^{-1}.

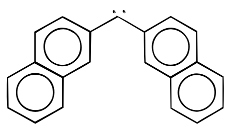
Introduction

Low-temperature matrix spectroscopy has greatly contributed to the understanding of geometric and electronic structure of carbenes, an important group of intermediates produced in many chemical reactions. Carbenes have very short (nanoseconds to 50 μs) lifetimes in the gas and liquid phase.[1−3] In a cryogenic matrix, however, friction greatly restricts molecular motion. Under these conditions, carbenes, once created by the photolysis with visible or UV light from their diazo, diazirine, and/or ketene precursors, are often persistent. Thus, prolonged studies are possible as long as the matrix is kept frozen.

Carbenes possess two nonbonding electrons and depending on their molecular structure may have either a singlet (S_0) or triplet (T_0) ground state. The energy separation between the lowest singlet states is small and the excitation energy relaxation between these states ($S_n \rightarrow S_0$) proceeds mainly via internal conversion on a picosecond time scale.[4] On the other hand, the energy separation between the T_0 and T_1 states is much larger and the radiative transition ($T_1 \rightarrow T_0$) can compete with nonradiative relaxation of the T_1 state. Hence, to this date, only carbenes with the triplet ground state have been studied by fluorescence emission spectroscopy in the visible spectral range.

In triplet carbenes, both triplet states, T_0 and T_1, involved in the $T_1 \rightarrow T_0$ fluorescence and $T_0 \rightarrow T_1$ absorption, even in the absence of external magnetic field, are split into three spin components.[5] In diaryl carbenes which contain only carbon and hydrogen atoms, the zero-field splitting (zfs) of triplet states originates from dipolar spin−spin interaction between unpaired electrons,[6] thus providing important information on the spatial distribution of these electrons. The conventional technique of the electron spin magnetic resonance (ESR) has been successfully used to determine the zfs parameters (D_0 and E_0) of many triplet carbenes in their ground state.[1] However, this technique cannot be used to study the short-lived (on a nanosecond time scale) excited T_1 states. The first approach to determine the zfs parameters of the excited state of triplet carbenes was to study the magnetic field effect on the fluorescence decays.[7,8] This indirect method has several limitations and has been applied to only a few carbenes.

Recently, we proposed and investigated a new method that can provide the zfs parameters *D* and *E* with great precision directly for both T_0 and T_1 states in the same experiment. The experiment is the hole burning on the (0,0) fluorescence excitation line[9] of triplet carbenes dissolved in low-temperature Shpolskii matrixes. This method has already been successfully applied to 2-naphthylphenylcarbene (2-NPC),[10,11] 2,2-dinaphthycarbene (2,2-DNC),[12] and 7*H*-benz[*de*]anthracen-7-ylidene (7-BAC).[13] The present contribution continues our recent hole-burning studies, extending them to the Z/cis conformer of 2,2-DNC.



Z/cis conformer of 2,2-DNC

This conformer dominates the fluorescence spectrum of 2,2-DNC dissolved in a low-temperature matrix of *n*-heptane. Because of the spectral position of the (0,0) line of the $T_0 \rightarrow T_1$ transition (the maximum of the main inhomogeneous band

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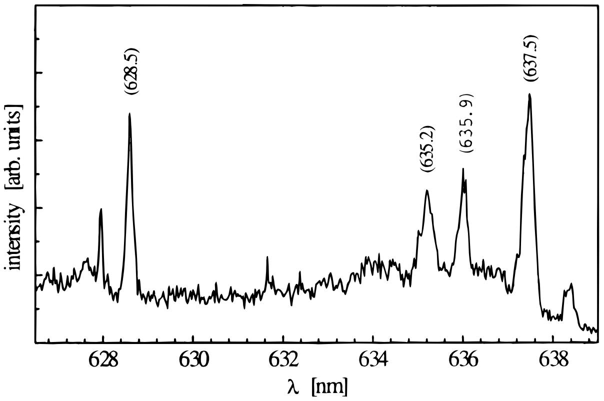

Figure 1. Inhomogeneous lines of the main sites of 2,2-DNC in *n*-heptane at 5 K in the (0,0) fluorescence excitation.

in *n*-heptane is at 637.5 nm, out of the lasing range of Rhodamine 6G) this conformer was not explored by hole burning in our previous work.[12]

Experimental Section

The 2,2-DNC sample was obtained in situ by photolysis of 2,2-dinaphthyldiazomethane[12] dissolved in *n*-hexane or *n*-heptane at 4.2 K. The precursor concentration was between 10^{-3} and 2×10^{-3} mol/L. Photolysis was performed with the 366 and 404 nm lines isolated from a low-pressure mercury lamp. All samples were degassed by the freeze−pump−thaw technique before being inserted into a liquid helium cryostat.

Hole-burning experiments were performed (in the Bordeaux laboratory) by using a single-mode dye laser Coherent CR 699−21, lasing within the spectral range of interest with Kiton Red and having 1−3 MHz frequency resolution and 30 GHz maximum scan width. The laser light intensity was stabilized by an electrooptic modulator Conoptics Lass-II. The fluorescence light, emitted from the sample, was collected by an achromatic lens and focused on the slit of a small monochromator. The monochromator was used to select the most intense vibronic lines of carbene, 1309−1388 and 1345−1376 cm^{-1} from the 0,0 origin of the fluorescence in *n*-hexane and in *n*-heptane, respectively. The scattered excitation light was further removed with a RG665 Schott glass filter. Fluorescence intensity was detected in the photon-counting mode by using a cooled RCA 31034-A02 photomultiplier.

Fluorescence decays were measured using the time-correlated single-photon-counting technique. The experimental setup (in the Warsaw laboratory) was the same as that already described in reference (12).

Results and Discussion

The low-energy part of the fluorescence excitation spectrum of 2,2-DNC in *n*-heptane at 5 K is presented in Figure 1. Several narrow bands identified with different (0,0) origins are observed. Spectral holes were burned within the inhomogeneous bands which have maxima at 637.5, 635.9, and 628.5 nm. The full widths at half-maximum (fwhm) of these bands were between 5 and 7 cm^{-1}. Typical spectra of detected holes are shown in Figures 2−4.

The spectra of holes burned within the 637.5 and 635.9 nm bands are similar; see Figures 2 and 3. They contain the central hole, with a depth reaching 30−40% and fwhm of 70 MHz; two holes symmetrically located on both sides of this central hole, 1.1 GHz away; and two pairs of holes, also symmetrically located with respect to the central hole; one pair on the low and the second on the high-energy side, 16.2 and 17.36 GHz away.

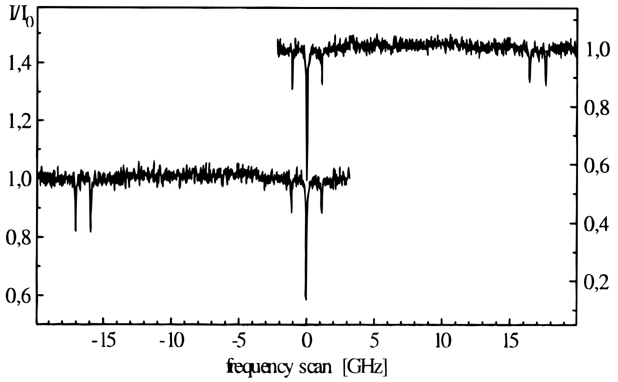

Figure 2. Spectrum of holes burned within the inhomogeneous profile of the (0,0) fluorescence excitation line (having a maximum at 637.5 nm) of 2,2-DNC in *n*-heptane at 1.7 K. The spectral positions of the holes are given with respect to the frequency of the laser burning light. The spectrum presented was obtained under the following experimental conditions: wavelength of the hole-burning light = 637.4 nm, burning intensity = 8 $\mathrm{mW/cm^2}$, and burning time = 180 s.

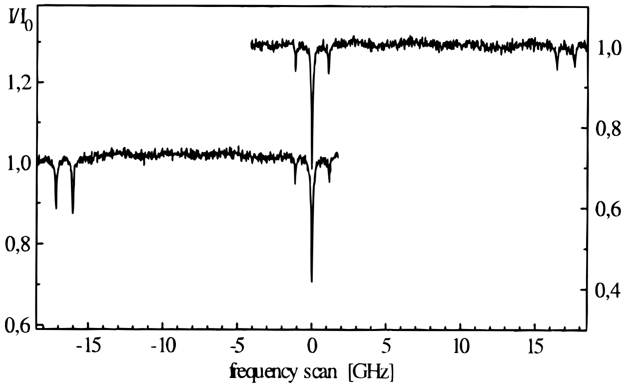

Figure 3. Spectrum of holes burned within the inhomogeneous profile of the (0,0) fluorescence excitation line (having a maximum at 635.9 nm) of 2,2-DNC in *n*-heptane at 1.7 K. The spectral positions of the holes are given with respect to the frequency of the laser burning light. The spectrum was obtained under the following experimental conditions: wavelength of the hole-burning light = 635.83 nm, burning intensity = 8 $\mathrm{mW/cm^2}$, and burning time = 15 min.

The hole-burning efficiency with the 628.5 nm line was some 4 orders of magnitude higher than that within the lower energy (0,0) bands. The typical spectrum of holes is also different, as shown in Figure 4. The central hole, at the frequency of burning light has two satellite holes on the low-energy side, 0.79 and 14.14 GHz away. A weak hole is also present on the high-energy side, 13.26 GHz away from the frequency of the central hole.

Furthermore, we burned holes within the (0,0) inhomogeneous fluorescence excitation band with maximum at 633.61 nm, attributed to the pseudo-Z/cis conformer of 2,2-DNC in *n*-hexane at 1.7 K. A typical hole spectrum is shown in Figure 5. It resembles the spectra of the same conformer in *n*-heptane, presented in Figures 2 and 3, although in *n*-hexane matrix the holes are broader. A typical fwhm of the central hole was larger than 200 MHz.

The spectra of holes presented in Figures 2, 3, and 5 can be explained with the energy level scheme presented in Figure 6. Both triplet states, T_0 and T_1 are split into three spin components, with the larger splitting in the ground state. Furthermore, we

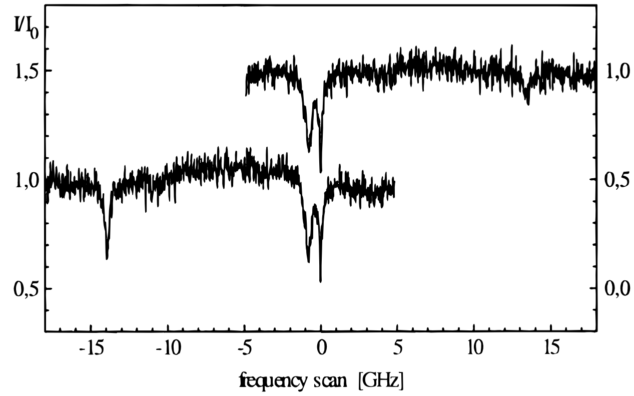

Figure 4. Spectrum of holes burned within the inhomogeneous profile of the (0,0) fluorescence excitation line (having a maximum at 628.5 nm) of 2,2-DNC in *n*-heptane at 1.7 K. The spectral positions of the holes are given with respect to the frequency of the laser burning light. The spectrum was obtained under the following experimental conditions: wavelength of the hole-burning light = 628.46 nm, burning intensity = 0.8 μW/cm^2, and burning time = 180 s.

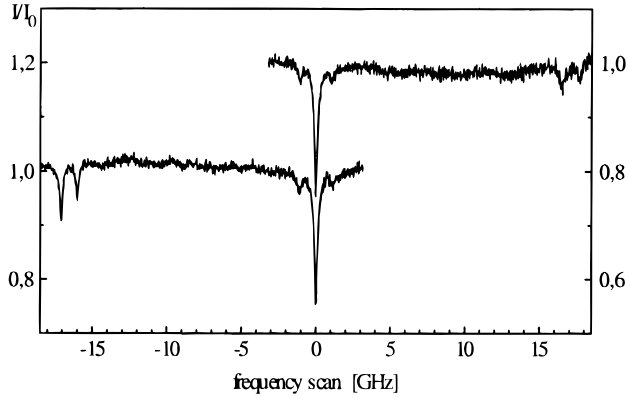

Figure 5. Spectrum of holes burned within the inhomogeneous profile of the (0,0) fluorescence excitation line (having a maximum at 633.7 nm) of 2,2-DNC in *n*-hexane at 1.7 K. The spectral positions of the holes are given with respect to the frequency of the laser burning light. The spectrum was obtained under the following experimental conditions: wavelength of the hole-burning light = 633.61 nm, burning intensity = 0.8 mW/cm^2, and burning time = 5 min.

assumed that the principal spin axes of the 2,2-DNC conformer under study are preserved when this molecule is excited from the T_0 to the T_1 state. Therefore, we assumed that the only allowed electronic transitions are those between the sublevels of the same spin component: $T_{0z} \rightarrow T_{1z}$, $T_{0y} \rightarrow T_{1y}$, and $T_{0x} \rightarrow T_{1x}$. This point will be discussed in more detail (vide infra). The hole-burning laser light can interact (be in resonance) only with three groups of carbenes, those with the same energy of the $T_{0x} \rightarrow T_{1x}$ transition (group 1), $T_{0y} \rightarrow T_{1y}$ (group 2), and $T_{0z} \rightarrow T_{1z}$ (group 3). The transitions corresponding to the laser burning light are indicated in Figure 6 by thick lines. If all three of these groups of carbene contribute, the expected spectrum of holes is shown at the bottom of Figure 6. It corresponds perfectly to the experimental spectrum (see Figures 2, 3, and 5). Let us now focus on some consequences of this model.

The absorption probability is proportional to $|\langle \varphi_g S_i | M | \varphi_e S_j \rangle|^2$, where φ_g and φ_e refer to the initial (ground) and final (excited) electronic wave functions, S_i and S_j are spin component wave functions in both states, and M is the dipole moment operator. The spin is insensitive to the electric field and thus we can easily transform this absorption probability into the formula $|\langle \varphi_g | M | \varphi_e \rangle|^2 \cdot |\langle S_i | S_j \rangle|^2$, which shows that the electronic transitions are possible only between those spin sublevels which have nonorthogonal directions of their principal spin axes. In the general case, when the principal spin directions are different in the ground and excited states, we can expect that each carbene would have nine possible transitions between the spin sublevels of the ground and excited states, and thus the spectrum of holes would be complicated.[12] In the other limit, when the principal spin axes are preserved in both, the T_0 and T_1 states, $\langle S_i | S_j \rangle \neq 0$ for $i = j$ only, the spectrum will be simple, resembling that at the bottom of Figure 6. An invariant direction of the principal spin axes *x*, *y*, and *z* is a characteristic feature of a compound that has C_{2v} symmetry. Therefore, we postulate that the Shpolskii matrixes of *n*-heptane and *n*-hexane force both the naphthalene rings of the pseudo-Z/cis conformer of 2,2-DNC to the same symmetry plane. This conclusion is a direct consequence of the simple pattern of burned holes.

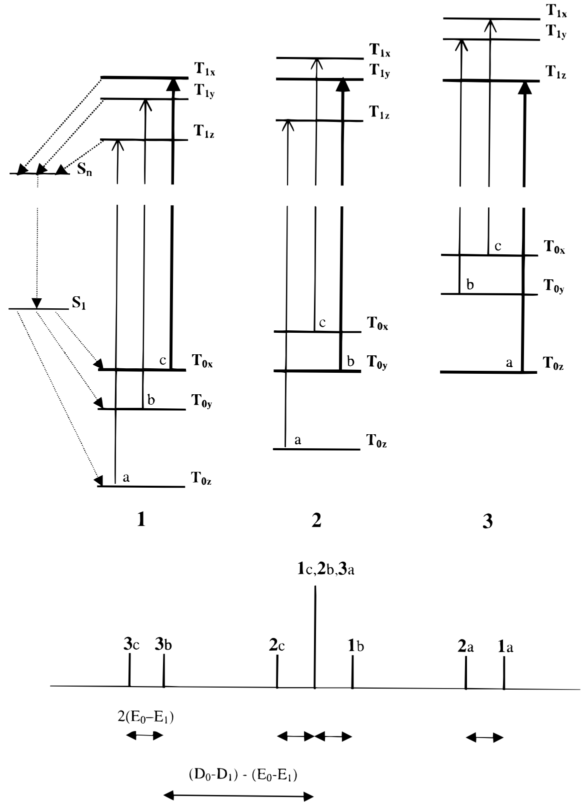

Figure 6. Energy level schemes and absorption transitions of 3 groups of carbenes which can contribute to the observed spectrum of holes. The thick lines indicate the transitions resonant with the frequency of the laser burning light. The predicted spectrum of holes with characteristic energy separations is shown at the bottom of the scheme.

It is also important to consider the hole-burning mechanism for the Z/cis conformer of 2,2-DNC. We were able to study the carbene of interest for several days without any loss of total fluorescence intensity. This observation indicates that hole-burning process does not have a photochemical origin. Whatever the burning mechanism, the hole depth should increase with the number of photons absorbed by carbenes. This number depends on the pathway of the excitation energy relaxation. There are two possible channels of nonradiative relaxation of the T_1 state, the internal conversion leading directly to the ground T_0 state and the intersystem crossing via the singlet states. The intersystem crossing channel consists of three steps: relaxation from the T_1 state to the lower energy singlet state, followed by internal conversion (within the singlet manifold) to the lowest energy S_1 state, and final step, intersystem crossing to the ground T_0 state. The former relaxation channel, triplet-to-triplet internal conversion, does not differentiate among the three groups of carbenes of interest. If this channel is dominant, the depths of satellite holes are expected to be the same. On the other hand, the intersystem crossing relaxation channel is known to populate selectively one of the spin sublevels of the ground state (the T_{0z}) as observed previously in the case of pseudo-E/trans conformers of 2-NPC[10,11] and 2,2-DNC.[12] A dominant intersystem crossing pathway in the relaxation of excitation energy would therefore favor carbenes from group 3 because these carbenes can efficiently absorb many photons and thus be burned. Carbenes from groups 1 and 2, when transferred to their T_{0z} sublevel (as the result of energy relaxation process via intersystem crossing pathway), are protected from absorbing any new burning photons. The spin−lattice relaxation process that restores the Boltzmann population of the spin sublevels is usually long at 1.7 K. The number of photons that can be absorbed by carbenes from groups 1 and 2 would be therefore much smaller than the number of photons absorbed by carbenes from group 3. Carbenes from group 3 contribute to the pair of satellite holes located on the low-energy side, and only these holes should be created if excitation energy relaxes via the intersystem crossing channel. The spectra of holes presented in Figures 2, 3, and 5 demonstrate that dominant relaxation channel of the Z/cis conformer of 2,2-DNC is the internal conversion, although relaxation via intersystem crossing is also important, especially for 2,2-DNC in *n*-hexane (Figure 5).

Important information about the excitation energy relaxation channels can be further provided by fluorescence decays. We fitted these decays by the sum of three exponential decays with the same preexponential factors, the dependence predicted for an independent decay of the three spin sublevels of the T_1 state.[3] For the inhomogeneous (0,0) bands with maxima at 637.5 and 635.9 nm of 2,2-DNC in *n*-heptane we found component decay times of 4.2, 11.6, and 11.6 ns (corresponding to decay rate constants of 23.8×10^7 and 8.6×10^7 s^{-1}). These rates indicate that one spin sublevel of the T_1 state is depopulated more rapidly than the other two. We propose that it is the T_{1z} spin sublevel. Thus, the T_{1x}, T_{1y}, and T_{1z} spin sublevels decay via the internal conversion with rate constants of 8.6×10^7 s^{-1}, and the T_{1z} sublevel via the intersystem crossing as well, with the rate constant for this process of 15.2×10^7 s^{-1}. Carbenes from group 3 can thus absorb more photons than those from groups 1 and 2, which explains the slightly larger depth of the satellite holes related to these carbenes (holes 3c and 3b in Figure 6). For the Z/cis conformer of 2,2-DNC in *n*-hexane (inhomogeneous (0,0) line at 633.7 nm) we found the decay components of 7.0, 7.0, and 15.6 ns[12] (corresponding to the decay rate constants of 14.3 $\times 10^7$ and 6.4×10^7 s^{-1}). Here, we propose that the three spin sublevels of the T_1 state are depopulated by the internal conversion channel with a rate constant of 6.4×10^7 s^{-1} and that two of them, T_{1x} and T_{1y}, are depopulated by the intersystem crossing pathway with the rate constant for this process of 7.9 $\times$ 10^7 s^{-1}. The intersystem crossing pathway selectively populates the T_{0z} spin sublevel and carbenes from groups 1 and 2 cannot absorb any new photon until the spin−lattice relaxation transfers them back to the T_{0x} and T_{0y} spin sublevels, respectively. Thus, carbenes from these groups can absorb burning photons less efficiently than carbenes from group 3 and the depth of holes 3c and 3b (Figure 6) is larger than that of the other satellite holes.

The spectral positions of holes provide information about the zfs of both states involved in the $T_0 \rightarrow T_1$ absorption. Unfortunately, due to the enforced C_{2v} symmetry of the Z/cis carbene conformer, the number of allowed transitions is limited and the hole-burning spectra yield information about the differences of the zfs parameters of the ground T_0 (D_0 and E_0) and excited T_1 (D_1 and E_1) states, only. For 2,2-DNC contributing to the inhomogeneous (0,0) band with maximum at 637.5 nm in *n*-heptane (Figure 2) we found

$$D_0 - D_1 = 16.74 \pm 0.02 \text{ GHz} = 0.558 \pm 0.001 \text{ cm}^{-1}$$

$$E_0 - E_1 = 0.55 \pm 0.02 \text{ GHz} = 0.0183 \pm 0.001 \text{ cm}^{-1}$$

For 2,2-DNC in the site at 635.9 nm in *n*-heptane (Figure 3) we found

$$D_0 - D_1 = 16.83 \pm 0.02 \text{ GHz} = 0.561 \pm 0.001 \text{ cm}^{-1}$$

$$E_0 - E_1 = 0.57 \pm 0.02 \text{ GHz} = 0.019 \pm 0.001 \text{ cm}^{-1}$$

For 2,2-DNC in the site at 633.7 nm in *n*-hexane we found

$$D_0 - D_1 = 16.80 \pm 0.02 \text{ GHz} = 0.560 \pm 0.001 \text{ cm}^{-1}$$

$$E_0 - E_1 = 0.535 \pm 0.02 \text{ GHz} = 0.0178 \pm 0.001 \text{ cm}^{-1}$$

The above data gave approximately the same value, around 0.56 cm^{-1}, for the difference of the zfs parameters ($D_0 - D_1$). This value can be compared with the corresponding data for the pseudo-E/trans conformer of 2,2-DNC in *n*-hexane, $D_0 - D_1 = 0.477 - 0.043$ cm^{-1} = 0.434 cm^{-1}, estimated in our previous paper.[12] The comparison of the $D_0 - D_1$ values for both conformers is consistent with the simple model taking into account the spin densities[14] that predicts that the Z/cis conformer has a larger zfs parameter D_0, and has a lower $T_0 - T_1$ transition energy than the E/trans conformer. The arguments presented earlier for 2-NPC[14] apply to the related carbene, 2,2-DNC, as well.

It is more difficult to propose a convincing interpretation of the hole structure burned within the inhomogeneous (0,0) line with maximum at 628.5 nm of 2,2-DNC in *n*-heptane, shown in Figure 4. Using the model presented in Figure 6, we can formally attribute the satellite hole at −14.14 GHz to 3c, that at −0.79 GHz to 2c, and that at +13.26 GHz to 2a. It is, however, difficult to explain the lack of other holes indicated in Figure 6. For example, the absence of hole 3b is unexpected. The pattern of observed holes can be easily explained if we assume that the D_0 value is negative. In this case, however, it would be difficult to understand why the sign changes when 2,2-DNC is transformed to the pseudo-E/trans conformer, where it is positive.[12] The mentioned formal attribution of holes gives

$$D_0 - D_1 = 13.70 \pm 0.02 \text{ GHz} = 0.433 \pm 0.001 \text{ cm}^{-1}$$

$$E_0 - E_1 = 0.395 \pm 0.02 \text{ GHz} = 0.013 \pm 0.001 \text{ cm}^{-1}$$

The above differences of the zfs parameters are smaller than those of the Z/cis conformer discussed in this work but are equal, within the experimental errors, to those for the pseudo-E/trans conformer of 2,2-DNC, where $D_0 - D_1 = 0.434 \pm 0.001$ cm^{-1} and $E_0 - E_1 = 0.012 \pm 0.001$ cm^{-1}.[12] Let us note that a structure of holes similar to that in Figure 4 has been previously observed for the pseudo-Z/cis conformer of 2-NPC.[10] In the case of 2-NPC, the pseudo-Z/cis conformer was unstable to light and subject to light-induced transformation to the pseudo-E/trans geometry.[15] Probably, the inhomogeneous (0,0) line at 628.5 nm corresponds also to a photosensitive form of 2,2-DNC and the observed spectrum of burned holes can be related to a conformer undergoing geometrical transformation. This work is in progress and the unstable character of the 2,2-DNC form giving rise to the 628.5 nm line will be a subject of forthcoming investigations.

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