Triplet-State Dynamics of C_{70}

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Electron-spin-echo experiments at 9 and 95 GHz on the triplet state of C_{70} in glassy matrices are reported. Analysis of the echo decays as a function of the time after laser excitation allows a complete description of the distinct population and decay of the substates of the lowest triplet state of this fullerene at 1.2 K. The observation of spin−lattice relaxation between the triplet sublevels reveals pseudorotation of the C_{70} molecule about its long axis on a time scale of microseconds even at such a low temperature. The fine-structure parameter D of triplet C_{70} is found to be positive.

Introduction

The high symmetry of the leading fullerenes C_{60} and C_{70} makes the study of the electronic and geometric structure of these molecules in their electronically excited states of particular interest. The lowest triplet state of C_{60} belongs to the T_{2g} irreducible representation under I_h symmetry. In line with the orbitally degenerate character of this state, a distortion and symmetry lowering of the molecule upon excitation is observed. The triplet sublevel degeneracy is fully lifted as expressed by the nonzero values of the fine-structure parameters D and E.[1] For C_{70}, the subject of the present paper, an axial fine-structure tensor would be compatible with the D_{5h} symmetry of the molecule and the nondegenerate A_2' orbital character of the lowest triplet state.[2,3] Experiments, however, show that also for C_{70} both D and E are nonzero.[1]

Up to now the triplet state of C_{70} has mainly been studied by electron-paramagnetic-resonance (EPR) spectroscopy at 9 GHz. Wasielewski et al. were the first to report on C_{70} in toluene at 5 K, for which they obtained $|D| = 155$ MHz and $|E| = 21$ MHz.[1] Similar values were found later for C_{70} in methylcyclohexane,[4] in toluene,[5] in poly(methyl methacrylate) (PMMA)[6] and in polystyrene[7] using time-resolved EPR, whereas an E value about twice as large was deduced from a pulsed optically detected magnetic-resonance experiment in zero field.[8] None of these experiments enabled a determination of the sign of D, which was assumed to be positive in refs 6 and 7 and negative in refs 4 and 5. The triplet EPR spectra of C_{70} show spin polarization that was interpreted in terms of a sublevel-selective triplet population leading to a non-Boltzmann population distribution. Less agreement exists concerning the values of the populating probabilities p_i ($i = x, y, z$) of the triplet sublevels. Ratios p_x:p_y:p_z (where z is the long molecular axis) of 1:0.95:0.85 for C_{70} in methylcyclohexane at 3 K,[4] 0.06:1:0.1 in toluene at 8 K,[5] and 0.03:0.03:1 in PMMA at 4 K[6] have been reported. Above about 10 K the EPR spectrum following pulsed laser excitation shows a time evolution that is governed by spin−lattice relaxation.[4−6] At lower temperatures the results are contradictory as yet. Wasielewski et al.,[1] using time-resolved EPR, detected at 9 K for C_{70} in toluene containing 10% poly(α-methylstyrene) a decay time of 51 ms at one magnetic field strength, which they related to the phosphorescence decay time of 53 ms measured at 77 K. On the other hand, Terazima et al.,[4] using time-resolved EPR as well, found for C_{70} in methylcyclohexane at 3 K sublevel decay rates of 1.7, 1.6, and 1.4 ms^{-1}, corresponding to a much shorter average lifetime of 0.65 ms. Finally Saal et al.[8] analyzed the decay of the phosphorescence of C_{70} in toluene between 1.2 and 77 K and concluded that the intrinsic decay rate of all three sublevels is the same and that the triplet lifetime is 47 ms.

In summary, the sublevel dynamics of triplet C_{70} at liquid helium temperatures seems anything but settled, and the selectivity of the population and the decay remains to be quantified. Since these data are most relevant in relation to the question of the electronic structure and distortion of C_{70} in the triplet state, we have investigated the dynamics, in both decalin/cyclohexane and toluene, by electron-spin-echo (ESE) detected EPR at X-band (9 GHz) and at W-band (95 GHz) microwave frequencies. It is found that at W-band and 1.2 K spin−lattice relaxation takes place from the $m_s = 1$ to the $m_s = -1$ triplet sublevel on the time scale of the triplet lifetime. As a result the decay of the spin-echo intensity as a function of the time after triplet formation depends strongly on the magnetic field in W-band. Assuming identical populating probabilities and decay rates for the nearly degenerate T_x and T_y substates, a model is presented that provides a quantitative description of the echo decays, both at W-band and at X-band microwave frequencies. Of the triplet substates, the T_z substate, which is found to be lowest in energy ($D > 0$), becomes preferentially populated upon optical excitation and decays fastest to the ground state. Largely similar behavior is observed for C_{70} in decalin/cyclohexane and in toluene.

Experimental Section

Highly purified C_{70} (>99.9%) was used, and experiments were performed on frozen solutions of C_{70} in decalin/cyclohexane (3:1 v/v) and in toluene. All experiments were performed at 1.2 K. The samples were excited by pulsed frequency-doubled Nd:YAG lasers, operating at 5 Hz with powers of about 25 mJ/pulse and a wavelength of 532 nm. For the W-band measurements a Quanta Ray DCR-2 laser was used and for the X-band measurements a Continuum Surelite I.

Electron-spin-echo experiments were performed at 9.67 GHz on a Bruker ESP 380 spectrometer and at 94.9 GHz on a home-built spectrometer.[9] Two-pulse echo sequences were applied

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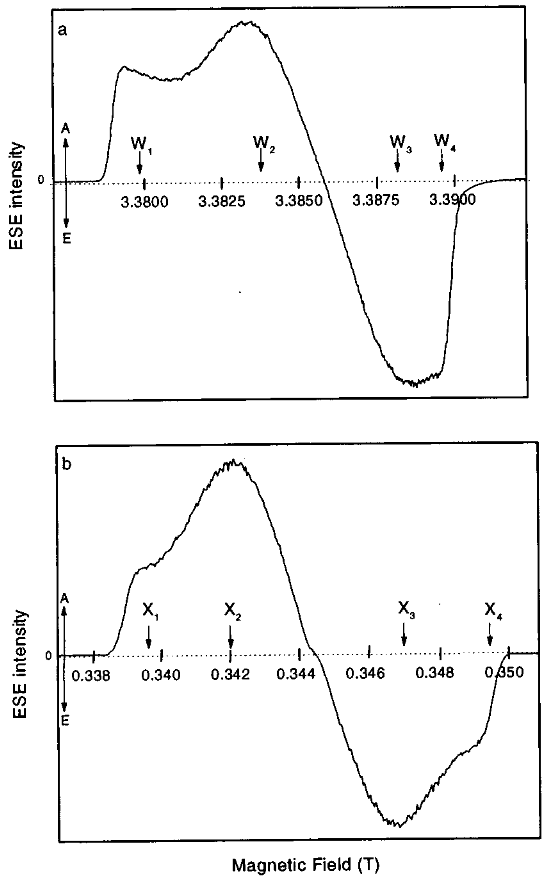

Figure 1. W-band (a) and X-band (b) ESE-detected EPR spectrum of C_{70} in decalin/cyclohexane at $t_d \approx 10$ μs and 1.2 K; "A" refers to absorption, "E" to emission.

at a delay time t_d after the laser flash. Spin echoes were detected as a function of the magnetic-field strength at a fixed t_d (ESE-detected EPR) and as a function of the delay time t_d at a fixed magnetic field.

Results

Figure 1 shows ESE-detected EPR spectra at two microwave frequencies of a solution of C_{70} in decalin/cyclohexane at 1.2 K measured shortly after laser excitation. The low-field side of both spectra is absorptive, the high-field side emissive. The intensity at the low- and the high-field edges derives from those molecules of the randomly oriented ensemble whose fine-structure z axis is parallel to the magnetic field, while the inner maxima derive from those molecules whose fine-structure x or y axis is parallel to the magnetic field. The mirror symmetry (apart from the sign) of the low- and high-field side of the X-band spectrum (Figure 1b) is lost in the W-band spectrum (Figure 1a) owing to the anisotropy of the g matrix.

In order to study the triplet-state dynamics, the ESE intensity has been monitored as a function of the time t_d after laser excitation at various magnetic-field strengths indicated by the arrows in Figure 1. The fields are marked X1 to X4 and W1 to W4 for X- and W-band, respectively. The results are represented in Figures 2 and 3. At X-band all decays can be well-described by monoexponential functions with about the same time constant, while more complex behavior is observed at W-band. The absorptive ESE signal at field W2 initially rises, passes through a maximum, and decays slowly. At both the fields W3 and W4, the initially emissive signal becomes absorptive after some tens of milliseconds before decaying slowly to zero. The distinct field dependence of the time profiles at W-band corresponds to a change of the ESE-detected EPR spectra on a 100 ms time scale, which is illustrated in Figure 4a. Whereas directly after triplet formation absorption and emission are balanced, after about 50 ms the spectrum has become purely absorptive and shows intensity predominantly at the high-field side.

For C_{70} in toluene, identical experiments have revealed comparable results that slightly deviate in a quantitative sense, as can be seen from Figure 4b.

Discussion

The variation of the ESE intensity with the delay time t_d at a particular magnetic field strength reflects the decay of the population difference of the two triplet sublevels connected by the microwaves. The echo intensity depends on the relative populating probabilities p_i and the decay rates k_i, where the subscript i refers to the triplet substates in high field ($i = 1, 0, -1$). For each orientation of the magnetic field with respect to the C_{70} molecule, the T_i states correspond to certain linear combinations of the zero-field states T_x, T_y, and T_z. The distribution of molecules among the substates may be influenced by spin−lattice relaxation.

First we consider C_{70} in decalin/cyclohexane. The decays observed in X-band (Figure 2) are in good approximation monoexponential for all magnetic fields, while most decays in W-band (Figure 3) reveal (at least) biexponential behavior. For both X- and W-band the high-field approximation applies (9.5 and 95 GHz compared to a fine-structure splitting of about 150 MHz), and therefore one expects identical transients at both microwave frequencies except for differences caused by a change in the spin−lattice relaxation rate with frequency. The shape of the W-band ESE-detected EPR spectrum at 1.2 K changes with the delay time t_d (Figure 4a), which indicates that under these conditions, of magnetic field and temperature, spin−lattice relaxation occurs on a time scale comparable to that of the triplet decay. Indeed, it is found that spin−lattice relaxation from the $m_s = 1$ to the $m_s = -1$ sublevel has to be taken into account in order to arrive at a consistent interpretation of the W-band transients at all magnetic fields.

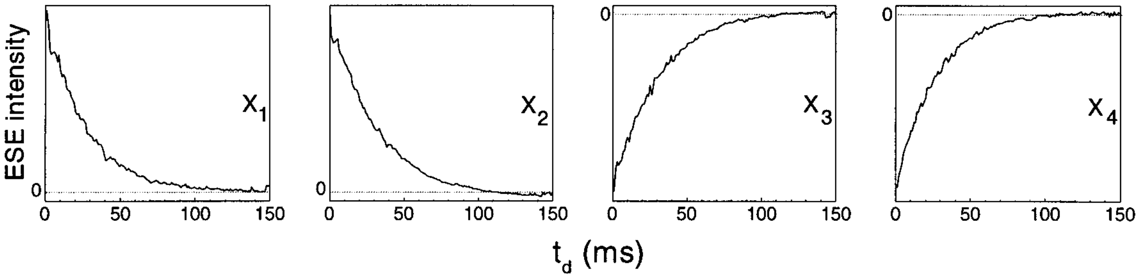

Figure 2. Time evolution of the echo intensity at X-band frequency for C_{70} in decalin/cyclohexane at 1.2 K as a function of the delay, t_d, of the first microwave pulse with respect to the laser flash at magnetic fields X_1 to X_4 indicated in Figure 1b.

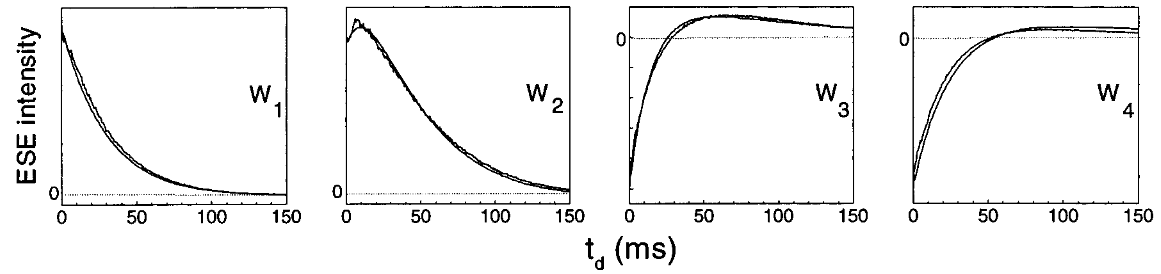

Figure 3. Time evolution of the echo intensity at W-band frequency for C_{70} in decalin/cyclohexane at 1.2 K as a function of the delay, t_d, of the first microwave pulse with respect to the laser flash at magnetic fileds W_1 to W_4 indicated in Figure 1a. The smooth curves are calculated according to eq 2 and the parameter values in Table 1.

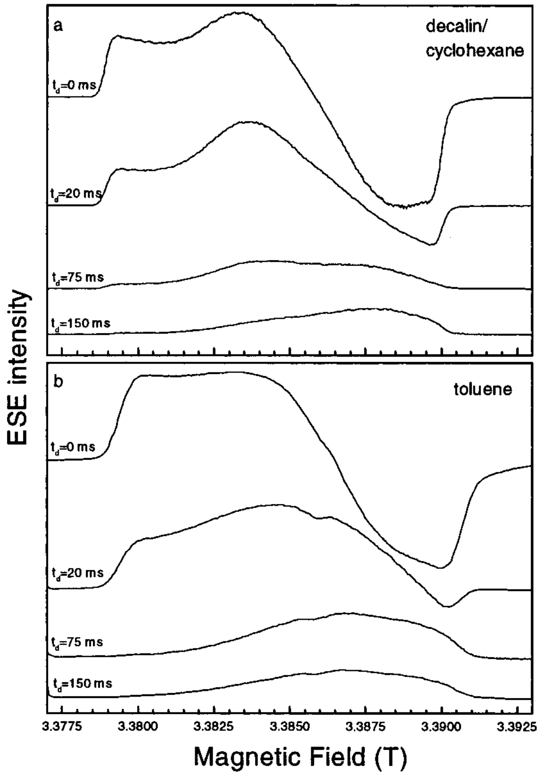

Figure 4. W-band ESE-detected EPR spectra of C_{70} in decalin/cyclohexane (a) and toluene (b) at 1.2 K for various delay times t_d with respect to the laser flash.

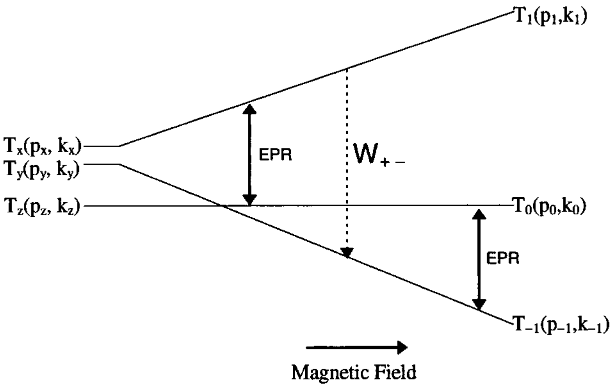

Figure 5. Schematic diagram of the triplet sublevels in zero and in magnetic field. Low- and high-field EPR transitions are indicated as well as the $\Delta m_s = 2$ downward spin−lattice relaxation.

The model used to analyze the kinetic data is illustrated in Figure 5 for a C_{70} molecule with its fine-structure principal z-axis parallel to the external magnetic field. In zero-field the T_z substate is found to be lowest in energy (vide infra). We assume that the decay rates in high field may be expressed in terms of the zero-field rates k_x, k_y, and k_z according to

$$k_i = \sum_{u=x,y,z} c_{iu}^2 k_u \quad (i = 1, 0, -1) \tag{1}$$

where the coefficients c_{iu} represent the mixing of the zero-field states. The $\Delta m_s = 2$ spin−lattice relaxation rate is indicated by W_{+-}. A similar relation is adopted between the relative populating probabilities p_i and p_u. (Note that these commonly used relations need not be true. If the zero-field states do not belong to different irreducible representations of the point group of the distorted molecule, interference terms will occur.[10]) In the quantitative analysis of the ESE decays we made two assumptions. First, only molecules with their fine-structure z-axis parallel to the magnetic field contribute at fields W_1, W_4, X_1, and X_4, while only molecules with their fine-structure x- or y-axis parallel to the magnetic field contribute at fields W_2, W_3, X_2, and X_3. Second, the substates T_x and T_y are assumed to have equal relative populating probabilities and decay rates. A D_{5h} symmetry would imply $p_x = p_y$ and $k_x = k_y$. The small value of the fine-structure parameter E indicates that upon triplet excitation the C_{70} molecule distorts only slightly from D_{5h} symmetry, which justifies the assumption. Experimentally we are, anyway, not able to resolve the tiny difference between x and y because the measurements involve a frozen solution of randomly oriented molecules. Within this model the following expressions hold for the decay of the echo intensities in W-band.

$$\begin{aligned}
&\text{at } W_1\text{: } I(t_d) \sim p_z\, e^{-k_z t_d} - p_x\, e^{-(k_x+W_{+-})t_d} \\
&\text{at } W_2\text{: } I(t_d) \sim 2\{p\, e^{-k t_d}\,(2 - e^{-W_{+-}t_d}) - p_x\, e^{-k_x t_d}\} \\
&\text{at } W_3\text{: } I(t_d) \sim 2\{p_x\, e^{-k_x t_d} - p\, e^{-(k+W_{+-})t_d}\} \\
&\text{at } W_4\text{: } I(t_d) \sim p_x\, e^{-k_x t_d}(2 - e^{-W_{+-}t_d}) - p_z\, e^{-k_z t_d}
\end{aligned} \tag{2}$$

where $p \equiv {}^1/_2(p_x + p_z)$ and $k \equiv {}^1/_2(k_x + k_z)$. The factor of 2 in the expressions for the fields W2 and W3 results from the fact that at these fields both molecules with their x-axis and molecules with their y-axis parallel to the magnetic field contribute to the echo. The same expressions, with $W_{+-} = 0$ apply to X-band, i.e., for X_1 to X_4. We are left with four parameters, p_z/p_x $(=p_z/p_y)$, k_z, k_x $(=k_y)$, and W_{+-}, which have been determined from a fit of the experimental W-band data to the above expressions. Subsequently, it is found that setting $W_{+-} = 0$ and keeping the other parameters fixed provides an adequate description of the decays at X-band. The latter data are particularly sensitive to k_z, and a simultaneous fit of the X-band and W-band decays, fixing W_{+-} at zero for X-band, only leaves an appreciable uncertainty with regard to the value

TABLE 1: Kinetic Data for C_{70} in Decalin/Cyclohexane and in Toluene at 1.2 K

	p_z/p_x	k_z (s^{-1})	k_x (s^{-1})	W_{+-} (s^{-1})
decalin/cyclohexane	7.6 ± 1.0	36.3 ± 2.6 (28 ± 2 ms)	10.9 ± 4.0 (92 ± 30 ms)	43.8 ± 5.8 (23 ± 3 ms)
toluene	4.6 ± 1.0	33.4 ± 2.2 (30 ± 3 ms)	13.1 ± 6.2 (76 ± 30 ms)	80.6 ± 22 (12 ± 3 ms)

of k_x. The parameter values that result for C_{70} in decalin/cyclohexane are summarized in Table 1.

The calculated echo decays based on the parameters for C_{70} in decalin/cyclohexane from Table 1 reproduce the experimental W-band data in all detail, as illustrated in Figure 3. Decays at fields W_1 and W_4 reflect molecules for which the magnetic field is parallel to the fine-structure z-axis (cf. Figure 5). For those molecules T_0 corresponds to T_z, which carries most of the population while decaying fastest. The population of T_1 decays about equally fast through spin−lattice relaxation, thereby increasing the population of T_{-1} that decays slowly. This explains the decay seen at the field W_1 (corresponding to the $T_1 \leftrightarrow T_0$ transition) and the zero-crossing at W_4 (corresponding to the $T_0 \leftrightarrow T_{-1}$ transition). The decays at fields W_2 and W_3 can be understood in a similar way by considering the molecules with the magnetic field along the fine-structure $x(y)$-axis. Both the early hump at W_2 and the zero-crossing at W_3 are caused by the fast spin−lattice relaxation from T_1 to T_{-1}. For X-band spin−lattice relaxation is negligible at 1.2 K and the decays at fields X_1 to X_4 are all dominated by the fast decay and large population of T_z. Zero-crossings at long decay times are not observed owing to the small population of T_x and T_y.

Similar results are obtained for C_{70} in toluene. Quantitative analysis (cf. Table 1) of the decays in this solvent, along the lines described for decalin/cyclohexane, reveals that the values of k_x and k_z are about the same (within the error margins) as in decalin/cyclohexane, while the spin−lattice relaxation in toluene is roughly twice as fast as in decalin/cyclohexane. In the aromatic solvent the intersystem crossing is a little less selective toward the T_z substate.

For triplet C_{70} the T_z substate (z refers to the long axis of C_{70}) is found to be lowest in energy, i.e., the fine-structure D parameter is positive. While the echo decays at X-band frequency as such would also be compatible with a negative D, the data at W-band frequency as well as the combination of X-band and W-band data are not. For a negative D, the X-band data would imply $k_z > k_x$ and those in W-band $k_z < k_x$. In addition, in order to reproduce the hump at field W_2 for negative D, a faster spin−lattice relaxation has to be assumed, which results in a faster rise at W_4 than at W_3, contrary to the experimental observation.

The use of W-band ESE spectroscopy at 1.2 K has allowed a quantitative analysis of the populating and decay of the lowest triplet state of C_{70}. Our results seem to provide insight into the confusing set of data presently available from the literature. The preferential population of the T_z sublevel is also observed for C_{70} in PMMA by Agostini et al.[6] These authors analyzed the line shape of the X-band EPR spectrum at 4 K and concluded an even smaller relative population of T_x and T_y than found presently. The analogy of our results in decalin/cyclohexane and toluene suggests that this difference probably is not a matrix-induced effect. It might well be that the line shape at X-band is not sensitive enough to p_x and p_y. Our decays at X-band are completely dominated by the population and decay of T_z, and only the decays at W-band allowed a determination of the population of T_x and T_y. The decay of transient X-band EPR signals at 8 K or higher reflects spin−lattice relaxation and does not provide information on the intrinsic dynamics of the uncoupled triplet sublevels.[4,5] The decay rates of the triplet sublevels in Table 1 correspond to an average lifetime of 51 ms of C_{70} in decalin/cyclohexane and in toluene. This value is consistent with the lifetime derived from phosphorescence decay measurements in toluene at 77 K, 53 ms[1] and 47 ms.[8] The sublevel decay rates reported by Terazima et al.[4] are incompatible with these data because they point to an average triplet lifetime of less than 1 ms. In contrast to our results, the decay of the phosphorescence has been interpreted in terms of equal decay rates of the triplet sublevels.[8] The analysis of such a decay suffers from many assumptions and parameters and may not be unique because the lifetimes of the sublevels do not differ by more than a factor of 3.

Finally we come back to the spin−lattice relaxation between T_1 and T_{-1} that shows up in the 95 GHz ESE experiments at 1.2 K. We propose that this spin−lattice relaxation is caused by pseudorotation of the C_{70} molecule around its long (z)-axis,[4−6] initially described by Closs et al. for triplet C_{60}.[11] The slight distortion of C_{70} from D_{5h} symmetry upon triplet excitation leads to equivalent minima in the potential energy as a function of the angle around the z-axis. Pseudorotation concerns the rotation of the magnetic axes related to the interconversion of C_{70} between the degenerate states. This dynamic Jahn−Teller effect introduces time dependence in the fine-structure part of the spin Hamiltonian: $H_s \sim E[S_x^2(t) - S_y^2(t)]$. The bilinear operators $S_x{}^2$ and $S_y{}^2$ may induce transitions between the Zeeman states T_1 and T_{-1}. In order to estimate the resulting relaxation rate W_{+-}, we assume that the relaxation concerns a direct process in which a single quantum is exchanged between the spin system and the phonon bath. The ratio between W_{+-}, determined by the spontaneous and stimulated emission, and W_{-+}, determined solely by the stimulated absorption, is given by the Boltzmann factor $e^{-\Delta E/kT}$, where ΔE represents the energy difference between T_1 and T_{-1}. When assuming that the time dependence of $ES_x{}^2(t)$ and $ES_y{}^2(t)$ is given by a random function fluctuating around an average value and is characterized by an autocorrelation function with a correlation time τ_c, the mean-square fluctuations of the transition probability at frequency ω (the frequency splitting of the levels T_1 and T_{-1}) may be expressed as[12]

$$W_{-+} = \frac{1}{\hbar^2}|\langle 1|ES_{x,y}^2| - 1\rangle|^2 \frac{2\tau_c}{1 + \omega_0^2\,\tau_c^2} \qquad (3)$$

A similar description has been reported for the self-trapped exciton in AgCl.[13] For an estimate of τ_c, the only unknown parameter in eq 3, we take the value of the triplet spin dephasing time T_2, which amounts to about a microsecond. We then calculate $W_{-+} \approx 12 \times 10^{-3}\ s^{-1}$ and, via the Boltzmann factor, $W_{+-} \approx 20\ s^{-1}$, which is of the right order of magnitude (cf. Table 1). The rate W_{+-} is determined by spontaneous emission (cf. a Boltzmann factor of ≈2000 at 95 GHz and 1.2 K), which explains that spin−lattice relaxation does not show up at 9.5 GHz and 1.2 K.

Conclusion

The application of 95 GHz electron-spin-echo spectroscopy has enabled a full description of the populating and decay of the triplet sublevels of C_{70} in glassy matrices at liquid helium temperatures. Spin−lattice relaxation from the $m_s = 1$ to the $m_s = -1$ sublevel, not relevant on the time scale of the triplet decay at 9.5 GHz, becomes significant at 95 GHz. The spin−lattice relaxation reflects the pseudorotation of the C_{70} molecule in the triplet state about its long axis on the time scale of microseconds at 1.2 K. At 9.5 GHz the echo decay as a function of the time after triplet formation is dominated by the T_z sublevel at all magnetic fields. At 95 GHz the spin−lattice relaxation causes a strong dependence of the echo decay on the magnetic field strength. Analysis of this variation reveals the distinct population and decay of the triplet substates. About 75% of the molecules that enter the triplet state upon excitation do so through the T_z sublevel. The decay to the ground state is about three times faster for molecules in T_z than for those in T_x of T_y. Results are largely similar for C_{70} in decalin/cyclohexane and in toluene. The lifetime of the triplet sublevel T_x (taken equal to that of T_y) amounts to 92 ± 30 ms and 76 ± 30 ms, and that of T_z to 28 ± 2 ms and 30 ± 3 ms in decalin/cyclohexane and toluene, respectively.

From the relative populating probabilities and the decay rates one calculates a steady-state population of T_z more than two times larger than that of T_x and T_y. Consequently, the transitions between the triplet sublevels should be observable in zero-field. Optical detection of such magnetic-resonance transitions is presently under study in our laboratory.

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