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Quantum beats in the recombination of radical ion pairs caused by hyperfine interaction in radical anions

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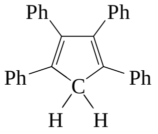
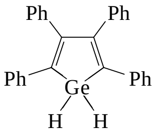
Quantum beats in the recombination fluorescence of 1,2,3,4-tetraphenylcyclopenta-1,3-diene and 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene radical anions have been detected and the hfc constants in these species determined.

Quantum beats in the recombination fluorescence of spin-correlated radical ion pairs are caused by the dynamic origin of the singlet–triplet (S–T) transitions and are induced by hyperfine[1] and Zeeman[2] interactions. The lifetime of such pairs formed in solution upon UV or ionizing irradiation typically lies in the nanosecond time scale. The investigation of quantum beats allows us to obtain unique information on the origin and transformations of these short-lived intermediates.

Unfortunately, well-resolved quantum beats were observed only in a few systems. In the case of the hfc mechanism the beats caused by hyperfine interactions were observed in radical cations;[1] however, their amplitudes were small. This restricts the usefulness of the method in quantitative studies. Here we report on clearly defined quantum beats in the recombination of radical ion pairs caused by hyperfine interactions in radical ions of 1,2,3,4-tetraphenylcyclopenta-1,3-diene **1** and 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene **2**.



1



2

Singlet radical ion pairs were generated by the irradiation of 10^{-3}–10^{-4} M solutions of **1** (**2**) in decane with X-ray pulses (duration 2 ns) and S–T beats were detected from the kinetics of recombination fluorescence. In the initial act of ionization a singlet pair (decane radical cation)/(free electron) with an average distance of several tens of angstroms is formed. Because of its high mobility the electron is captured by a molecule of **1** (**2**) almost instantly while the whole of the solvent remains free. Therefore, in the nanosecond region a decane radical cation and a radical anion A^- participate in geminate recombination.

The experimentally measured value – the intensity of recombination fluorescence $I(t)$ – is proportional to the product function $F(t)$ describing the kinetics of the geminate recombination of radical pairs and the probability of finding a system in a singlet state $W_S(t)$:

$$I(t) \quad F(t)\,W_S(t)$$

To separate the S–T beats it is necessary to exclude beforehand the unknown, rapidly descending function $F(t)$. For these purposes the ratio $I_H(t)/I_0(t)$ [where $I_H(t)$ was measured in a high magnetic field and $I_0(t)$ was measured in a zero magnetic field] was analysed.

The results of the experiment are shown in Figure 1. Clearly defined damped oscillations of similar shape but different periods were observed. The shapes of the curves are almost the same in fields 400–3000 G. Thus, the hyperfine interaction rather than a difference in g-factors of the radicals is the reason for the beats. Since the oscillation periods in the two systems under study are different they must be caused by hyperfine interaction in radical anions $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ rather than in the decane radical cation. The disappearance of the oscillations after the substitution of hydrogen atoms attached to the germanium in **2** to the methyl groups is an additional argument in support of this conclusion.

Table 1 hfc Constants in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ radical anions.

Radical anion	Method	hfc constant/G	Reference
$\mathbf{1}^{\cdot-}$	quantum beats	25.0±0.3	this work
$\mathbf{1}^{\cdot-}$	EPR	25.3	4
$\mathbf{2}^{\cdot-}$	quantum beats	15.5±0.3	this work

Computer simulation showed that the shape of the beats is well described in terms of the hyperfine interaction of an electron with two equivalent protons of CH_2 (GeH_2) moieties. The oscillations are damped because of spin relaxation processes. In this case in a high field the frequency of S–T oscillation is equal to a, and in zero field it is equal to $1.5a$, where a is the hfc constant with two equivalent hydrogens.[3] The results of hfc constant simulation are given in Table 1.

Good agreement of the hfc constant in $\mathbf{1}^{\cdot-}$ obtained by us and by the EPR method in THF solution[4] demonstrates the excellent ability of the method of quantum beats to determine parameters of the EPR spectra when short lifetime of paramagnetic species excludes their detection by conventional EPR spectroscopy.

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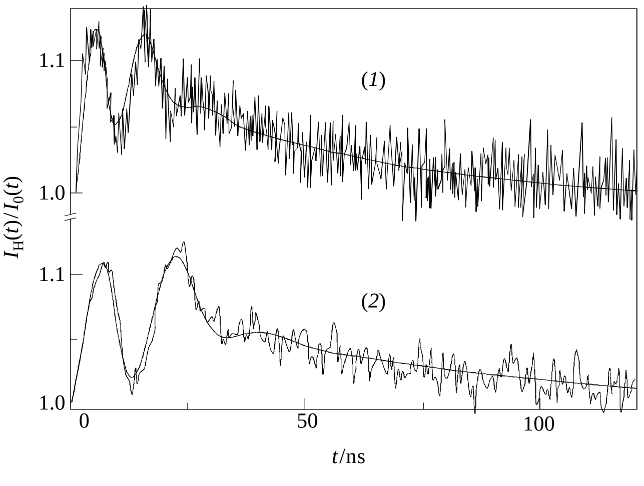

Figure 1 Ratio of $I_H(t)/I_0(t)$ for the decay of recombination fluorescence in high and in zero fields for solutions of **1** and **2** in decane. The solid lines are calculations taking into account the hyperfine interaction with two equivalent protons of CH_2 (GeH_2) moieties and the damping beats are caused by spin relaxation.

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