

# Paramagnetic relaxation of cyclohexane radical cation in solution as measured by the method of time-resolved magnetic field effect

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The method of time-resolved magnetic field effect was applied to measure the spin–lattice relaxation time  $T_1$  for radical cations of a number of cycloalkanes in *n*-hexane solution at room temperature. The  $T_1$  value for the Jahn–Teller active cyclohexane radical cation was found to be approximately 9 ns which was substantially shorter than typical values for organic radical ions. Based upon the similarity of effects that various factors had on the spin–lattice relaxation rate of the cyclohexane radical cation and the benzene radical anion it was proposed that the spin–orbital interaction made the predominant contribution to the relaxation of both radicals.

## Introduction

Alkane radical cations are known to be the key primary intermediates in the radiolysis of alkane solutions.<sup>1,2</sup> The numerous attempts to visualize these radical cations in solution by the EPR technique showed that this was possible only in a few cases with a highly sensitive variant of the method such as optically detected EPR (OD EPR).<sup>2,3</sup> The short lifetime of the radical cations was believed to be the main reason for their elusiveness. Indeed, experiments on pulsed radiolysis showed that the lifetime of radical cations of many alkanes in solutions was typically less than or equal to several tens of nanoseconds.<sup>1,2</sup> Similar ranges of the lifetimes of these particles were provided by MARY (MAGnetic field effect on Reaction Yield) spectroscopy.<sup>4</sup>

At the same time, the radical cations of cyclohexane or *trans*-decalin were also never observed in solution using the OD EPR technique even though their lifetimes were found by conductivity measurements to be within the submicrosecond range.<sup>5</sup> The failure in observing these radical cations using the magnetic resonance technique may be explained by their fast paramagnetic relaxation. For the *trans*-decalin radical cation, this assumption was confirmed by MARY spectroscopy. The spin–lattice relaxation time of this radical was found to be about 7 ns.<sup>6</sup> It was argued that a possible reason for the fast relaxation of the *trans*-decalin radical cation is a strong spin–orbital interaction due to the accidental degeneration of the electronic levels of this particle.

A hypothesis for the significant role of spin–orbital interactions in radicals with degenerate ground states was first put forward to account for the abnormally wide lines in the EPR spectra of the radical anions of aromatic molecules of a highly symmetrical structure, e.g., benzene or coronene.<sup>7–11</sup> It was found that these radical anions had unusually short paramagnetic relaxation times,  $T_1$  and  $T_2$ , that amounted to about 100 ns. These values were found to be weakly dependent on solvent, temperature and magnetic field strength.<sup>8</sup> According to theoretical estimations, such a short paramagnetic relaxation time could not be assigned to typical relaxation mechanisms such as the modulation of the hyperfine coupling (hfc) or *g*-tensor components of the radicals, or the spin–rotational interaction.<sup>8–11</sup>

Although experimentally, the abnormally fast relaxation of the benzene radical anion was revealed more than 40 years ago, a theory quantitatively describing the relaxation in symmetrical radical ions has not yet been developed. However, this anomaly is likely to concern the degeneration of the ground electronic state of a radical having the geometrical structure of the parent close-shell molecule. The degeneracy is known to vanish, according to the Jahn–Teller effect, due to distortion of the radical structure and lowering of the symmetry. This distortion, however, can result in several radical conformations of the same or nearly the same energy. At not-too-low temperatures, the radical undergoes fast transitions between these conformations, because the barriers for these transitions are not high.<sup>12,13</sup> It is presumed that in transient states with the higher symmetry, the recovery of the degeneration of the electronic ground state of the radical causes a spin–orbital interaction, which results in spin–lattice relaxation.<sup>8–11</sup> This hypothesis is also supported by the fact that breaking the symmetry of an aromatic molecule by alkyl substitutions decreases significantly the relaxation rate.<sup>8</sup> In the presence of such perturbation, the split states can again become degenerate only due to thermally activated fluctuation of either a solvent or radical structure.

The present paper reports on the experimental evidence for a very fast paramagnetic relaxation of the cyclohexane radical cation, whose rate appears to be abnormally high for organic radical ions and exceeds by an order of magnitude the relaxation rate for the benzene radical anion. The measurement of the spin–lattice relaxation time was performed by the method of time-resolved magnetic field effect (TRMFE) in the recombination fluorescence of the spin-correlated radical ion pairs.<sup>14,15</sup> To explain the fast relaxation, we have studied the influences of the alkyl substituents in the cyclohexane ring as well as electron self-exchange and magnetic field strength on the relaxation rate.

## Experimental

The luminescence of *n*-hexane solutions was detected by a single photon counting technique using an X-ray fluorimeter described elsewhere.<sup>16</sup> The duration of the ionizing pulse was about 2 ns. The light was collected using an optical bandpass

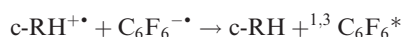
filter (260–390 nm). The sample cuvette was constructed to avoid the irradiation of quartz parts of the cuvette and to minimize the background luminescence.

To decrease the influence of instrumental drift, the fluorescence decays were registered for periods of 250 s, alternatively with and without the external magnetic field. Zero magnetic field was adjusted to within  $\pm 0.05$  mT, high field was up to 1 T.

*n*-Hexane ("Reactiv", Russia, 99%) was stirred with concentrated sulfuric acid, washed with water, passed several times through a 1 m column of activated alumina and stored over sodium. With gas chromatography we revealed that *n*-hexane contained 2-methylpentane (0.2%) and 3-methylpentane (0.5%) as the main impurities. Other impurities amounted to 0.05% and were not identified. The presence of the isomers was believed to have no significant influence on the results obtained. *cis*-Decalin, *trans*-decalin, methylcyclohexane, ethylcyclohexane, propylcyclohexane, *iso*-propylcyclohexane, *tert*-butylcyclohexane, and *cis*-1,2-dimethylcyclohexane were received from Aldrich and passed through a 0.5 m column of activated alumina before use. Hexafluorobenzene (Aldrich, 99%) and *para*-terphenyl-*d*<sub>14</sub> (Aldrich, 98%) were used as received. The solutions were degassed by repeated freeze–pump–thaw cycles. All measurements were made at  $293 \pm 0.5$  K.

## Description of the approach

In the present work, *n*-hexane solutions of a number cycloalkanes (c-RH) listed in Table 1 in the concentration range 0.03–0.3 M with addition of 0.01 M hexafluorobenzene as the luminophor were studied. In the solutions, X-rays generate the primary singlet correlated pairs of the *n*-hexane radical cation and excess electrons that transform subsequently to the secondary radical ion pairs. The ionization potentials of *n*-hexane, hexafluorobenzene and cyclohexane in the gas phase are 10.16 eV, 9.9 eV and 9.88 eV, respectively, while other cycloalkanes used have lower ionization potentials.<sup>17</sup> Under these conditions, the *n*-hexane radical cations transfer their positive charge to the molecules of the added c-RH within several nanoseconds to form c-RH<sup>+</sup>• species. Radical anions C<sub>6</sub>F<sub>6</sub><sup>•−</sup> are formed in subnanosecond time domains due to the high mobility of excess electrons in alkanes. The secondary radical ion pairs recombine and the excited states of luminophor are formed according to the reaction:



The spin multiplicity of the excited product and thus delayed fluorescence intensity are determined by the dynamics of the spin state of the radical ion pair (c-RH<sup>+</sup>•)/(C<sub>6</sub>F<sub>6</sub><sup>•−</sup>). Because of the high rate of the secondary radical ion formation the contribution of the solvent radical cation to spin dynamics is not significant.

**Table 1** Relaxation times of radical ions obtained by simulating the experimental TRMFE curves. In simulation, the value of the hfc constant in C<sub>6</sub>F<sub>6</sub><sup>•−</sup> was assumed to be 13.4 mT, a fraction of singlet-correlated pairs  $\theta$  was varied to within  $0.25 \pm 0.02$

Radical ion	$T_1/\text{ns}$	$T_2 = T_0/\text{ns}$
Hexafluorobenzene <sup>•−</sup>	$350 \pm 15$	$15 \pm 5$
<i>cis</i> -Decalin <sup>•+</sup>	$390 \pm 15$	$10 \pm 5$
<i>trans</i> -Decalin <sup>•+</sup>	$14 \pm 3$	$5 \pm 2$
<i>cyclo</i> -Hexane <sup>•+</sup>	$9 \pm 2$	$9 \pm 2$
Ethylcyclohexane <sup>•+</sup>	$21 \pm 3$	$10 \pm 5$
Propylcyclohexane <sup>•+</sup>	$38 \pm 4$	$7 \pm 3$
Methylcyclohexane <sup>•+</sup>	$57 \pm 10$	$5 \pm 2$
<i>cis</i> -1,2-Dimethylcyclohexane <sup>•+</sup>	$280 \pm 20$	$20 \pm 5$
<i>iso</i> -Propylcyclohexane <sup>•+</sup>	$280 \pm 20$	$20 \pm 5$
<i>tert</i> -Butylcyclohexane <sup>•+</sup>	$590 \pm 20$	$10 \pm 5$

It is known that in alkane solutions, at short luminophor fluorescence times, the decay of the delayed fluorescence intensity  $I(t)$  brought about by geminate recombination of radical ion pairs obeys the equation:

$$I(t) \propto F(t) \left[ \theta \rho_{\text{ss}}(t) + \frac{1}{4}(1 - \theta) \right] \quad (1)$$

where  $F(t)$  is the recombination rate of radical ion pairs,  $\theta$  is the fraction of pairs originating from the singlet-correlated state,  $\rho_{\text{ss}}(t)$  is the population of the singlet state of these pairs.<sup>14,15</sup> Experimental results on TRMFE are usually presented and analysed as a ratio:

$$\frac{I_B(t)}{I_0(t)} = \frac{\theta \rho_{\text{ss}}^B(t) + \frac{1}{4}(1 - \theta)}{\theta \rho_{\text{ss}}^0(t) + \frac{1}{4}(1 - \theta)} \quad (2)$$

that does not depend on the inexactly known function  $F(t)$ . In this equation, the indices *B* and 0 correspond to the measurements made at high and zero magnetic fields, respectively.

For many cases, the evolution of the spin population of the singlet state of a radical pair in high and zero magnetic fields can be described by the equations<sup>15</sup>

$$\rho_{\text{ss}}^B(t) = \frac{1}{4} + \frac{1}{4}e^{-\frac{t}{T_1}} + \frac{1}{2}e^{-\frac{t}{T_2}}G_c^B(t)G_a^B(t) \quad (3)$$

$$\rho_{\text{ss}}^0(t) = \frac{1}{4} + \frac{3}{4}e^{-\frac{t}{T_0}}G_c^0(t)G_a^0(t) \quad (4)$$

where the indices *a* and *c* refer to the radical anion and radical cation, respectively,  $G^{0,B}(t)$  are functions determined by the hfc constants and *g*-factors of radical ions,  $1/T_1 = 1/T_{1c} + 1/T_{1a}$  and  $1/T_2 = 1/T_{2c} + 1/T_{2a}$  are sums of the rates of spin–lattice and phase relaxation of the radical ions in high field,  $1/T_0 = 1/T_{0c} + 1/T_{0a}$  is the parameter to describe the phase relaxation in zero field.

As shown in ref. 18 eqns. (3) and (4) should be replaced by more complex ones if it is necessary to take into account the transformation of the EPR spectrum of radical ions during the spin state evolution. This transformation may occur, *e.g.*, due to change of conformation of a radical ion or charge transfer to another molecule. Note, that the effect of the electron self-exchange in the limiting cases of slow and fast spectral exchange may be described using eqns. (3) and (4) by the same way as the phase relaxation, *i.e.*, in terms of parameters  $T_2$  and  $T_0$ .<sup>18,19</sup>

The shape of the curve of the TRMFE in various regions is determined by the different parameters of a radical ion pair. If the *g*-value difference between the radical ions is not large, the magnetic field effect first increases with time, since  $\rho_{\text{ss}}(t)$  decay due to the singlet–triplet mixing caused by phase relaxation and hfc in radicals is faster in zero magnetic field. Further, the effect decreases due to the loss of spin coherence between radical ions in the pair because of spin–lattice relaxation.<sup>14,18</sup>

It follows from the relationships (eqns. (2)–(4)) that the most favorable for measuring the spin–lattice relaxation time is the condition  $T_0 \sim T_2 \ll T_1$ . Then, at times  $t \gg T_2$ , the magnetic field effect will be approximately described by the following equation:

$$\frac{I_B(t)}{I_0(t)} \approx 1 + \theta e^{-\frac{t}{T_1}} \quad (5)$$

Thus, provided there is a high rate of phase relaxation in a radical pair, irrespective of a particular mechanism of relaxation, the TRMFE curve decays exponentially with time  $T_1$ . This approach has already been used to study the paramagnetic relaxation of radical ions of a series of aromatic and olefin hydrocarbons.<sup>20</sup>

In the (c-RH<sup>+</sup>•)/(C<sub>6</sub>F<sub>6</sub><sup>•−</sup>) radical ion pairs studied in the present work, the fast S–T<sub>0</sub> transitions in high field and the

S–T ones in zero field are realized due to electron self-exchange of the radical ions. In the case of  $\text{C}_6\text{F}_6^{\bullet-}$ , because of comparatively large values of the hfc constant in the radical, the rate of the electron self-exchange corresponds to slow spectral exchange.<sup>21</sup> Therefore, the phase relaxation rate is approximately equal to the self-exchange one. Under the conditions of our experiments, the self-exchange reaction should provide the  $T_2$  value for the radical anion to be about 20 ns.<sup>4</sup> Calculating functions  $G_a^{B,0}(t)$  for the  $\text{C}_6\text{F}_6^{\bullet-}$  radical anion, we assumed that the EPR spectrum of this radical exhibited a resolved hyperfine structure determined by the hfc between the unpaired electron and six equivalent  $^{19}\text{F}$  nuclei with the constant 13.4 mT as reported in ref. 22. An explicit expression for the corresponding  $G_a^{B,0}(t)$  functions is given in ref. 15.

As to radical cations  $\text{c-RH}^{+\bullet}$ , studied in this work, most of them are likely to participate in the electron self-exchange with the rate determined by diffusion collisions. This assumption is supported by both the existence of highly mobile holes in the neat cyclic alkanes<sup>5</sup> and the direct measurements of the self-exchange rate for *cis*-decalin radical cation in dilute solution.<sup>6</sup> In our experimental conditions, at a concentration of about 0.1 M, the electron self-exchange is expected to cause significant broadening and overlapping of spectral lines in the EPR spectra of  $\text{c-RH}^{+\bullet}$  which display characteristic splitting of about 5 mT in low-temperature matrices.<sup>12,13</sup> At room temperature, the conformational transitions are sure to be an additional channel of hfc averaging in these radical cations.<sup>6</sup> The aforementioned factors concerning the radical cations would obviously cause a complication of the calculation procedure needed for the exact description of spin dynamics. As a first approximation, we have assumed that the hfc contribution of the radical cation can be neglected in the calculation of a particular form of  $G_c^{B,0}(t)$ . In other words, we put  $G_c^{B,0}(t) = 1$ , while the influence of the incompletely averaged hfc has been incorporated by varying parameters  $T_2$  and  $T_0$ .

With the use of these approximations, we reached satisfactory agreement between the calculated curves and the experimental ones. As illustrated below, variations in the procedures of taking into consideration the contribution of hfc in  $\text{c-RH}^{+\bullet}$  resulted only in deviations within an increasing part of the TRMFE curve and had no effect on the accuracy of the determination of  $T_1$ . It should be also noted that for most cases, the time of phase relaxation in  $\text{c-RH}^{+\bullet}$  was found to be substantially shorter than that of spin–lattice relaxation and to amount to units of nanoseconds. Such a short  $T_2$  value should be considered as additional evidence of essential contribution of unresolved hyperfine structure in radical cation to singlet–triplet mixing in the radical ion pairs.

In a number of experiments, *para*-terphenyl- $d_{14}$  (*p*-TP) was used as an acceptor of positive and/or negative charges. The ionization potential and the electron affinity of the *p*-TP molecule were about 7.7 and 0.7 eV, respectively.<sup>17</sup> The contribution of *p*-TP radical ions to the spin evolution of a radical pair was described in terms of a semiclassical approximation.<sup>19</sup> In the present work, the second moments,  $\sigma_{a,c}$ , of the EPR spectra of the  $\text{p-TP}^{+\bullet}$  and  $\text{p-TP}^{\bullet-}$  radical ions were considered to be equal. The  $\sigma_a$  value was calculated using the hfc constants for the *para*-terphenyl- $h_{14}$  radical anion given in ref. 23. For this case the explicit expression for  $G_{a,c}^{B,0}(t)$  functions was reported elsewhere.<sup>18,19</sup>

In simulations we also assumed that the phase relaxation times in high and zero magnetic fields were equal, *i.e.*,  $T_0 = T_2$ . We also neglected the difference between the *g*-factors of partners in radical ion pairs. These approximations did not introduce appreciable errors to the calculated curves of magnetic field effects and to the evaluated  $T_1$  values, because this difference is not large and could affect the curves only at times shorter than the phase relaxation time.

Note, that the possible contribution of *n*-hexane radical cation to the spin evolution was considered to be unimportant

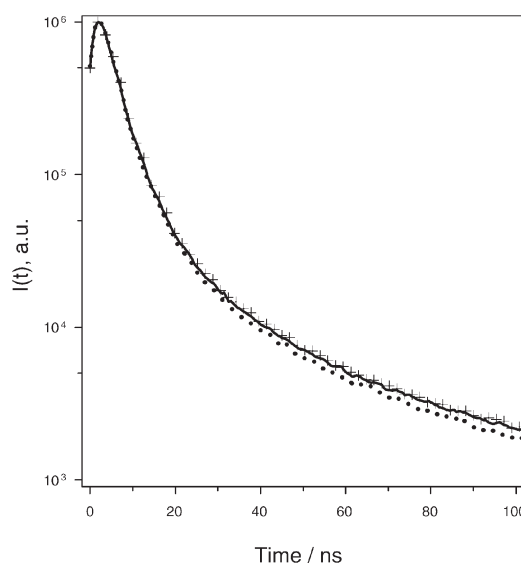
because of its fast transformation to the  $\text{c-RH}^{+\bullet}$ . Nevertheless, this contribution could increase to some extent the rate of the singlet–triplet evolution because the EPR spectrum width of the primary radical cation was sufficiently large, at about 5 mT.<sup>12</sup> However, we did not consider in detail this additional channel of S–T transitions when modelling magnetic field effects, it seemed to be responsible for a slightly higher value of parameter  $\theta$  as compared to the data reported in ref. 18.

## Results

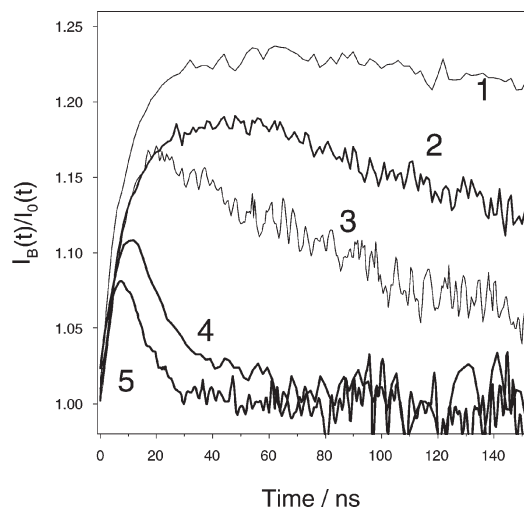
Fig. 1 shows the kinetics of the delayed fluorescence decays for *n*-hexane solutions of 0.01 M  $\text{C}_6\text{F}_6$  with the addition of 0.1 M of *cis*-decalin, *trans*-decalin, and cyclohexane. All the curves are normalized so that their maxima are equal. This approximately coincides with the normalization to the dose absorbed by solution. As follows from the figure, the kinetics curves are actually very close, which testifies to the similarity of the recombination processes of radical ion pairs in all these cases. For other *c*-RH used in the present work, the fluorescence decay kinetics are also close to those presented in Fig. 1.

Fig. 2 shows the TRMFE curves obtained for *n*-hexane solutions with the addition of various acceptors in a magnetic field  $B = 1$  T. Curve 1 shows the magnetic field effect for a solution of  $10^{-3}$  M *p*-TP. The other curves show the effects for the 0.01 M  $\text{C}_6\text{F}_6$  solutions with the addition of  $10^{-3}$  M *p*-TP (curve 2), 0.1 M *cis*-decalin (curve 3), 0.1 M *trans*-decalin (curve 4), and 0.1 M cyclohexane (curve 5).

For the solution containing *p*-TP only, the long time part of TRMFE is determined by spin dynamics in the  $\text{p-TP}^{\bullet-}/\text{p-TP}^{+\bullet}$  pairs. According to ref. 14, the times of spin–lattice relaxation of the *p*-TP radical ions are in the microsecond range. Hence, the magnetic field effect curve decays slowly over time. An initial increase of curve 1 occurs due to the hfc and the phase relaxation of the solvent radical cation whose capture time is 20–30 ns for the *p*-TP concentration used. In the solution containing both *p*-TP and  $\text{C}_6\text{F}_6$  the TRMFE curve is determined, at longer times, by the radical pairs  $\text{C}_6\text{F}_6^{\bullet-}/\text{p-TP}^{+\bullet}$ , because, according to ref. 21, the  $\text{p-TP}^{\bullet-}$  radical anion transfers an unpaired electron to the  $\text{C}_6\text{F}_6$  molecule on their first encounter in solution. As shown in curve 2 of Fig. 2 the decay of TRMFE in the  $\text{C}_6\text{F}_6^{\bullet-}/\text{p-TP}^{+\bullet}$  radical pairs is faster than that shown by curve 1. This can be obviously assigned to a faster spin–lattice relaxation of the  $\text{C}_6\text{F}_6^{\bullet-}$  radical anion as compared to  $\text{p-TP}^{\bullet-}$ . Curve 3 in Fig. 2 shows that replacing  $\text{p-TP}^{+\bullet}$  by *cis*-decalin



**Fig. 1** Decays of the delayed fluorescence for *n*-hexane solutions of  $10^{-2}$  M  $\text{C}_6\text{F}_6$  with the addition of 0.1 M *cis*-decalin (solid line), 0.1 M *trans*-decalin (dotted curve) and 0.1 M cyclohexane (crosshairs).

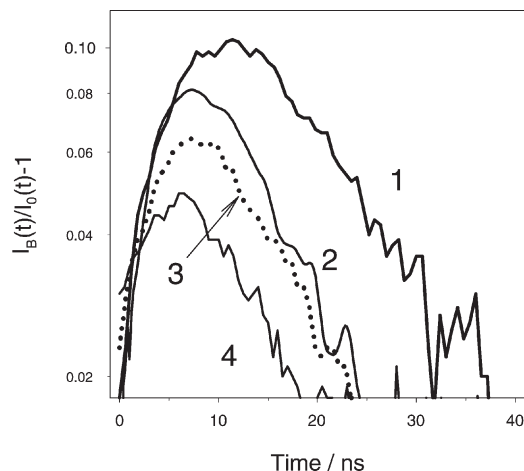


**Fig. 2** TRMFE curves in a magnetic field of 1 T for *n*-hexane solutions of: (1)  $10^{-3}$  M *p*-TP-*d*<sub>14</sub>; (2) 0.01 M C<sub>6</sub>F<sub>6</sub> +  $10^{-3}$  M *p*-TP-*d*<sub>14</sub>; (3) 0.01 M C<sub>6</sub>F<sub>6</sub> + 0.1 M *cis*-decalin; (4) 0.01 M C<sub>6</sub>F<sub>6</sub> + 0.1 M *trans*-decalin; (5) 0.01 M C<sub>6</sub>F<sub>6</sub> + 0.1 M cyclohexane.

radical cation in the radical pair involving the C<sub>6</sub>F<sub>6</sub><sup>•+</sup> leads to additional increase in the rate of spin–lattice relaxation. For the solutions containing *trans*-decalin and cyclohexane, the decay rate of magnetic field effect curves increases still further, which indicates a higher rate of the spin–lattice relaxation of the radical cation of these cycloalkanes. In the case of *trans*-decalin radical cation, this is in agreement with the data reported in ref. 6.

Fig. 3 shows in semilogarithmic coordinates the TRMFE curves obtained in *n*-hexane solution of 0.01 M C<sub>6</sub>F<sub>6</sub> with the addition of 0.03 M cyclohexane in a field of 1 T (curve 1), 0.1 M cyclohexane in a field of 1 T (curve 2; the same as curve 3 in Fig. 2), 0.1 M cyclohexane in a field of 0.1 T (scatter plot 3), and 0.3 M cyclohexane in a field of 0.1 T (curve 4). It is readily seen in accordance with eqn. (5), that the decay of magnetic field effect curve becomes monoexponential at longer times. These curves also indicate that the decay due to the spin–lattice relaxation of the cyclohexane radical cation depends weakly on magnetic field strength and cyclohexane concentration.

The increase in the magnitude of TRMFE curves with the decrease in concentration of cyclohexane may be attributed to the delay in the formation of the secondary radical cations.

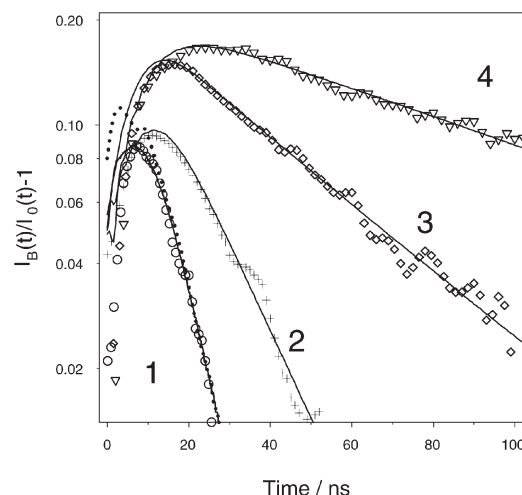


**Fig. 3** Semilogarithmic plots of TRMFE curves, obtained in  $10^{-2}$  M C<sub>6</sub>F<sub>6</sub> hexane solutions with the addition of 0.03 M cyclohexane in a field of 1 T (curve 1), 0.1 M cyclohexane in a field of 1 T (curve 2, coincides with curve 3 in Fig. 2), 0.1 M cyclohexane in a field of 0.1 T (dotted curve 3) and 0.3 M cyclohexane in a field of 1 T (curve 4).

At the lowest concentration of the solute the radical cation is formed with a delay of several nanoseconds, which is comparable with its paramagnetic relaxation time. In this case, the primary solvent holes with longer  $T_1$  have enough time to contribute substantially to the singlet–triplet mixing and results in a higher magnitude of TRMFE. After formation of the cyclohexane radical cation, the spin–lattice relaxation with short  $T_1$  takes place and the TRMFE curve decays with the same rate as in other cases. On the other hand, as the cyclohexane concentration increases to 0.3 M, the contribution of solvent holes to spin evolution becomes negligible. Besides, some narrowing of the EPR spectrum of the cyclohexane radical cation is expected due to a faster self-exchange reaction. As a result, the rate of S–T<sub>0</sub> transitions decreases whilst the value of  $T_1$  remains almost the same. In this case, the magnitude of the TRMFE curve should tend to diminish.

Fig. 4 shows in semilogarithmic coordinates the experimental curves (scatter plots) of the TRMFE obtained for *n*-hexane solutions of 0.01 M C<sub>6</sub>F<sub>6</sub> with the addition of cyclohexane (curve 1), ethylcyclohexane (curve 2), methylcyclohexane (curve 3), and *iso*-propylcyclohexane (curve 4) at concentrations of 0.1 M at a field of 1 T. Fig. 4 also shows the calculated curves of magnetic field effects (solid lines) obtained from eqns. (1)–(4) according to the model described in the previous section. Table 1 lists the optimum values for the paramagnetic relaxation times of radical ions in the field  $B = 1$  T, which have been used for the modelling.

Since the decay of magnetic field effect was determined by the spin–lattice relaxation of both radical cations and radical anions, the relaxation times of individual c-RH radical cations were found using the following procedure. First, we measured the rate of the decay of TRMFE for the pairs *p*-TP<sup>•+</sup>/*p*-TP<sup>•-</sup> within the range of 0–2 μs. Assuming that in these pairs the relaxation rates for both the radical cation and anion were equal, the value  $T_1 = 4200 \pm 150$  ns for the *p*-TP<sup>•+</sup> radical cation was obtained, which was in excellent agreement with the data reported by Brocklehurst.<sup>14</sup> Further, we simulated the TRMFE curve for hexane solutions containing both 0.01 M C<sub>6</sub>F<sub>6</sub> and  $10^{-3}$  M *p*-TP using the above  $T_1$  value for *p*-TP<sup>•+</sup>. Therefore, for the C<sub>6</sub>F<sub>6</sub><sup>•+</sup> in the field  $B = 1$  T, we derived that  $T_1 = 350 \pm 15$  ns. This value was used for simulations of the TRMFE curve obtained for c-RH/C<sub>6</sub>F<sub>6</sub> solutions in the field



**Fig. 4** Semilogarithmic plots of the experimental (scatter) and the calculated (lines) curves of TRMFE obtained for *n*-hexane solutions of  $10^{-2}$  M C<sub>6</sub>F<sub>6</sub> with the addition of 0.1 M cyclohexane (curve 1), 0.1 M ethylcyclohexane (curve 2), 0.1 M methylcyclohexane (curve 3) and 0.1 M *iso*-propylcyclohexane (curve 4) in a field of 1 T. The dotted curve was calculated for the case of cyclohexane with the  $T_1$  value given in Table 1 under the assumption that the unpaired electron in cyclohexane radical cation couples to 6 equivalent protons with the hfc constant  $a = 4.3$  mT.

$B = 1$  T. In the same manner the value of phase relaxation time  $T_2 = 15 \pm 5$  ns for the  $C_6F_6^{\bullet-}$  was determined.

Note, that when modelling TRMFE curves in the cyclohexane solution, the best agreement between the calculated and experimental data was achieved for  $T_1 \approx T_2$ . In other cases, it was necessary to assume that  $T_2 < T_1$ . In the simulation of all the TRMFE curves the  $\theta$  parameter was varied to within  $0.25 \pm 0.02$ .

As was mentioned in the previous section, the  $T_1$  values for  $c\text{-RH}^{+\bullet}$  were obtained in the framework of the model, in which the contribution of hfc in the radical cations was taken into account indirectly via the parameters  $T_2$  and  $T_0$ . For the cyclohexane solution, Fig. 4 also presents the calculated curve (dashed line) obtained with the same value of  $T_1$ , while the  $G_c^{B,0}(t)$  functions were derived for resolved EPR spectrum of the cyclohexane radical cation when the unpaired electron couples to six equivalent protons with the hfc constant being equal to 4.3 mT.<sup>12,13</sup> As follows from Fig. 4, the difference in these two ways of considering hfc in the radical cations manifests itself only at short times, without noticeable effect on the accuracy of the determination of spin–lattice relaxation time for the radicals.

## Discussion

The available data indicate that at room temperature, in neat *cis*- and *trans*-decalins, the lifetimes of their radical cations are hundreds of nanoseconds.<sup>5</sup> At the same time, the alkane radical cation is believed to have a longer lifetime diluted in other alkanes with a higher ionization potential.<sup>1</sup> As follows from Fig. 1, the time history of the processes resulting in the excitation of luminophor in the hexane solutions is almost the same for various cycloalkanes. Thus, it is reasonable to conclude that the lifetimes of the radical cations of all the studied cycloalkanes are also large enough.

Consequently, the fast decay of the TRMFE curves in the case of the solutions of cyclohexane and its derivatives is actually determined by the loss of spin correlation in the  $(c\text{-RH}^{+\bullet})/(C_6F_6^{\bullet-})$  radical pairs rather than by the decay of  $c\text{-RH}^{+\bullet}$  or by the disappearance of magnetosensitive fluorescence at the background of some luminescence insensitive to the magnetic field. This is also confirmed by a good agreement between our results for the *trans*-decalin radical cation and those obtained by MARY spectroscopy.<sup>6</sup> Indeed, as reported,<sup>6</sup> the spin–lattice relaxation time of *trans*-decalin radical cation is 7 ns. The re-evaluated data of that work according to a more accurate theory<sup>24</sup> will provide a value of about 14 ns, which coincides with the  $T_1$  value given in Table 1.

It is the modulation of hfc constants due to either the electron self-exchange or transitions between various Jahn–Teller distorted structures of the ground state that should be examined primarily as the reason for very fast spin–lattice relaxation of cyclohexane radical cation. In this case, spin–lattice relaxation is known to be described using the Redfield theory. When a fast spectral exchange condition  $(\gamma\Delta\tau_c)^2 \ll 1$  is fulfilled the rate of spin–lattice relaxation in a field  $B$  can be evaluated from the relationship<sup>25</sup>

$$\frac{1}{T_1} = \frac{2(\gamma\Delta)^2\tau_c}{1 + (\gamma B)^2\tau_c^2}, \quad (6)$$

Here  $\Delta$  is the mean-square value of the perturbation causing relaxation transitions,  $\tau_c$  is the correlation time of the perturbation, and  $\gamma$  is the gyromagnetic ratio. If a condition of slow spectral exchange,  $(\gamma\Delta\tau_c)^2 > 1$  is valid, the exchange is considered not to contribute markedly to the spin–lattice relaxation in high magnetic field.

From low temperature studies, it is known that the EPR spectrum of the cyclohexane radical cation at the low rate of transitions between the Jahn–Teller distorted structures is

determined by hfc constants of 8.5, 3.4, 1.4 mT with three pairs of equivalent protons, respectively.<sup>12</sup> Assuming for approximation that  $\Delta$  is equal to the second moment of the EPR spectrum, in the case of cyclohexane radical cations the value of  $\Delta$  is about 6.5 mT.

To estimate the contribution of the electron self-exchange reaction for the cyclohexane radical cations to the spin–lattice relaxation, it should be taken into account that the reaction is controlled by diffusional collisions. Thus, the rate constant of the reaction in *n*-hexane is expected to be about  $(1\text{--}2) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ . One can estimate that the increase in the cyclohexane concentration from 0.03 M to 0.3 M should result in the decrease in the typical exchange time  $\tau_c$  from about 2 ns to 0.2 ns. With the above value of  $\Delta$ , the lowest value of  $\tau_c$  may be considered as corresponding to fast spectral exchange. Eqn. (6) for  $\tau_c = 0.2$  ns gives  $T_1 \approx 4700$  ns in a magnetic field  $B = 1$  T. Therefore, the electron self-exchange reaction for the cyclohexane radical cations will not contribute to the spin–lattice relaxation appreciably. This conclusion is also supported by Fig. 3, which demonstrates that a change in the cyclohexane concentration as large as an order of magnitude does not result in a noticeable change in TRMFE curve decay.

As to the contribution of very fast transitions between Jahn–Teller distorted structures, one has to take into account that, according to eqn. (6), fast spectral exchange provides the maximum of the relaxation rate when  $\gamma B\tau_c = 1$ . For magnetic field  $B = 1$  T the corresponding value of  $\tau_c$  is about 6 ps. In the case of cyclohexane radical cations using this value for  $\tau_c$  and 6.5 mT for  $\Delta$  one can obtain the shortest expected value of the spin–lattice relaxation time of about  $T_1^* = 130$  ns. Since the measured  $T_1$  is an order of magnitude shorter than  $T_1^*$ , we conclude that the modulation of the hfc constants is not responsible for fast radical cation relaxation under our experimental conditions.

It can also be shown that the contribution of the modulation of the  $g$ -factor anisotropy in the case of cyclohexane radical cation is negligible despite the fact that this radical has a relatively high value of the  $g$ -factor (2.0069).<sup>13</sup> Besides, using the known relationships for the rate of spin–lattice relaxation due to spin–rotational interaction,<sup>26</sup> one can readily demonstrate that its contribution is also negligible.

As for the other cycloalkanes studied, their radical cations have lower values of hfc constants and the  $g$ -tensor shift.<sup>13</sup> Thus, all the relaxation mechanisms just discussed are also not capable of providing a  $T_1$  value shorter than 130 ns in a field of 1 T.

It follows from the data in Table 1 that the alkanes studied can be divided into two groups differing qualitatively in the rate of spin–lattice relaxation. The first group includes cyclohexane, *trans*-decalin, methyl-, ethyl-, and propylcyclohexane. The relaxation time of the radical cations of these compounds is much shorter than  $T_1^*$ , which indicates a predominant contribution of a specific relaxation mechanism having no relation to the modulation of hfc constants, the anisotropy of the  $g$ -factor or spin–rotational interaction. The second group involves all the other cycloalkanes. For this group, the contribution of this specific mechanism of paramagnetic relaxation is not so obvious.

Qualitatively, the process of spin–lattice relaxation of the cyclohexane radical cation has much in common with that of the benzene radical anion. These radicals have abnormally high spin–lattice relaxation rates, which weakly depend on field strength and decrease after the introduction of substituents into the ring. This allows us to conclude that the mechanisms of relaxation of these two Jahn–Teller active radical ions are similar and relate closely to a strong spin–orbital interaction arising from the accidental recovery of the degeneracy of singly occupied molecular orbitals (SOMO) of the radicals. In this case, a much higher relaxation rate of cyclohexane radical cation as compared to benzene anion correlates with the

larger shift of the  $g$ -factor, which clearly indicates increasing importance of spin–orbital interaction.

At the same time, as shown in ref. 27 the radical ions of aromatic and saturated cyclic hydrocarbons are dramatically different with respect to the influence of alkyl substituents on the distribution of electron and spin densities in the SOMO of a radical ion. For the benzene radical anion, such a substituent introduces a relatively small perturbation into the  $\pi$ -system of an aromatic ring without changing the character of its conjugation. In the case of cycloalkane radical cations ( $\sigma$ -radicals) the atomic orbitals of the alkyl substituent are considerably involved in the SOMO of the radicals.

Note that in the case of alkylsubstituted cycloalkanes a parallel may be drawn between our data and that obtained in low temperature EPR experiments. In radical cations of  $n$ -alkyl substituted cyclohexanes, having shorter relaxation times, the  $n$ -alkyl groups are located in an asymmetrical position with respect to SOMO of the ring structure.<sup>13</sup> In this case, there is a possibility for transition between two conformations differing in relative location of the alkyl fragment. In contrast to this, *iso*-propyl and *tert*-butyl fragments providing for much longer  $T_1$  times are in the symmetrical position. These branched fragments contain about 80% of spin density<sup>13</sup> and stabilize the electronic structure to a greater extent thus diminishing the possibility of attaining the degeneracy of electronic states of the radical cations.

At the same time, a fascinating problem arises from comparison of radical cations with  $n$ -alkyl substituents. The analogy with benzene would lead us to assume that perturbation of the electronic levels due to ethyl or propyl fragments should exceed that for the methyl group, and thus, the relaxation rate should decrease, while the real situation is the reverse. To gain a greater insight into the problem described, quantum-chemical calculations of the geometry and electronic structure of radical cations and of the dynamics of their conformation transitions is required, as well as the development of the theory of paramagnetic relaxation in  $\sigma$ -radicals in degenerate electronic states.

## Conclusions

The time-resolved magnetic field effect (TRMFE) in the  $n$ -hexane solutions of cyclohexane with addition of perfluorobenzene decays rapidly with time, independent of field strength and the rate of degenerate electron exchange of the cyclohexane radical cation. At the same time, the decay rate substantially decreases after the introduction of substituents into the cyclohexane ring. The analysis shows that the observed decay of the TRMFE curve takes place due to the loss of spin correlation in radical ion pairs including the cycloalkane radical cation because of the fast spin–lattice relaxation of the latter. The spin–lattice relaxation time of the cyclohexane radical cation as estimated from the modelling of TRMFE curves is  $9 \pm 2$  ns. The estimates indicate that the modulation of  $h\nu$  or the  $g$ -tensor as well as the spin–rotational interaction fail to provide the relaxation observed. Although in the case of methyl- and ethyl-substituted cyclohexanes the relaxation rate decreases, it is still too high to be explained by conventional mechanisms.

The observed peculiarities of the paramagnetic relaxation of the cyclohexane radical cation are similar to those observed for the benzene radical anion. Thus, the relaxation mechanisms for these Jahn–Teller active species are likely to be similar, and the spin–orbital interaction plays a decisive role in both cases.

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