Temperature dependence of EPR spectrum of 2-trifluoromethylnitrobenzene radical anion in acetonitrile*

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Temperature dependence of the EPR spectrum of 2-trifluoromethylnitrobenzene radical anion in anhydrous acetonitrile in the temperature range $217 \text{ K} \le T \le 296$ K was studied and simulated. Temperature-dependent dynamic modulation of the fluorine isotropic hyperfine structure is caused by slow hindered rotation of CF_3 group with an activation energy of $E_F^* = 36.5 \pm 0.5$ kJ mol^{-1}, which is the highest value for motions in π-type free radicals studied to date.

Key words: radical anions, isotropic hyperfine interaction, dynamic modulation, activation parameters, hindered rotation, slow exchange, EPR spectroscopy.

Among π-radical anions of substituted nitrobenzenes, 2-trifluoromethylnitrobenzene radical anion ($2\text{-}CF_3C_6H_4NO_2^{\bullet -}$, **1**) has the most asymmetric structure. The CF_3 group is near the NO_2 group; as a consequence, internal rotation of the former in the fragment —$(F_3C)C{=}C(NO_2)$— is hindered and the EPR spectrum of radical anion **1** exhibits a characteristic strong dynamic modulation of the hyperfine structure (HFS). The EPR spectrum of radical anion **1** in MeCN containing traces of water (no temperature measurements were carried out) was first reported in studies,[1,2] but the character of dynamic modulation of the HFS remained unclear, so even the constants of hyperfine coupling (HFC) with ^{19}F nuclei cannot be considered reliable.

In a DMF—water mixture the CF_3 group experiences fast rotation. The dynamic characteristics of the process make the radical anion **1** a highly sensitive spin probe capable of detecting stoichiometric structurization of the solvation cage.[3] Similar data on structurization of acetone—water and DMSO—water mixtures were obtained independently in dielectric spectroscopy studies[4,5] where the theory of the effect is also based on the simulation of local molecular rotational relaxation mechanisms in the liquid phase,[6] being in good agreement with the results of a recent quantum chemical analysis of molecular association in DMSO—water mixtures.[7]

In this work we studied the intramolecular dynamics in radical anion **1** in anhydrous MeCN.

Experimental

Radical anion **1** was generated under oxygen-free conditions in anhydrous MeCN by electrochemical reduction of 0.001 *M* solution of a depolarizer (2-trifluoromethylnitrobenzene) on a mercury cathode (supporting electrolyte 0.05 *M* Bu_4NClO_4) in the temperature range $217 \text{ K} \le T \le 296$ K. X-Band EPR spectra were measured (operating frequency $\nu = 9.762667 \cdot 10^9$ Hz) with a Bruker ESP-300 double-cavity radiospectrometer equipped with a Bruker B-ST 100/700 temperature accessory.

For data processing, the EPR spectra were represented as 4096-point numerical arrays. Numerical simulation of the EPR spectra was carried out using original Object Pascal optimization code.

Results and Discussion

The experimental EPR spectra of radical anion **1** at different temperatures and corresponding simulated spectra are shown in Fig. 1. The spectra obtained at the outermost points of the temperature interval are strongly different. Temperature variation within the range under study causes monotonic and reversible changes in the spectral line shape. Changes in the HFS correspond to a monotonic transition from equilibrium orientation (see Fig. 1, $T = 217.8$ K) to slow hindered rotation of the CF_3 group.

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* Dedicated to the memory of Academician V. A. Koptyug on the occasion of the 75th anniversary of his birth.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 926—931, June, 2006.

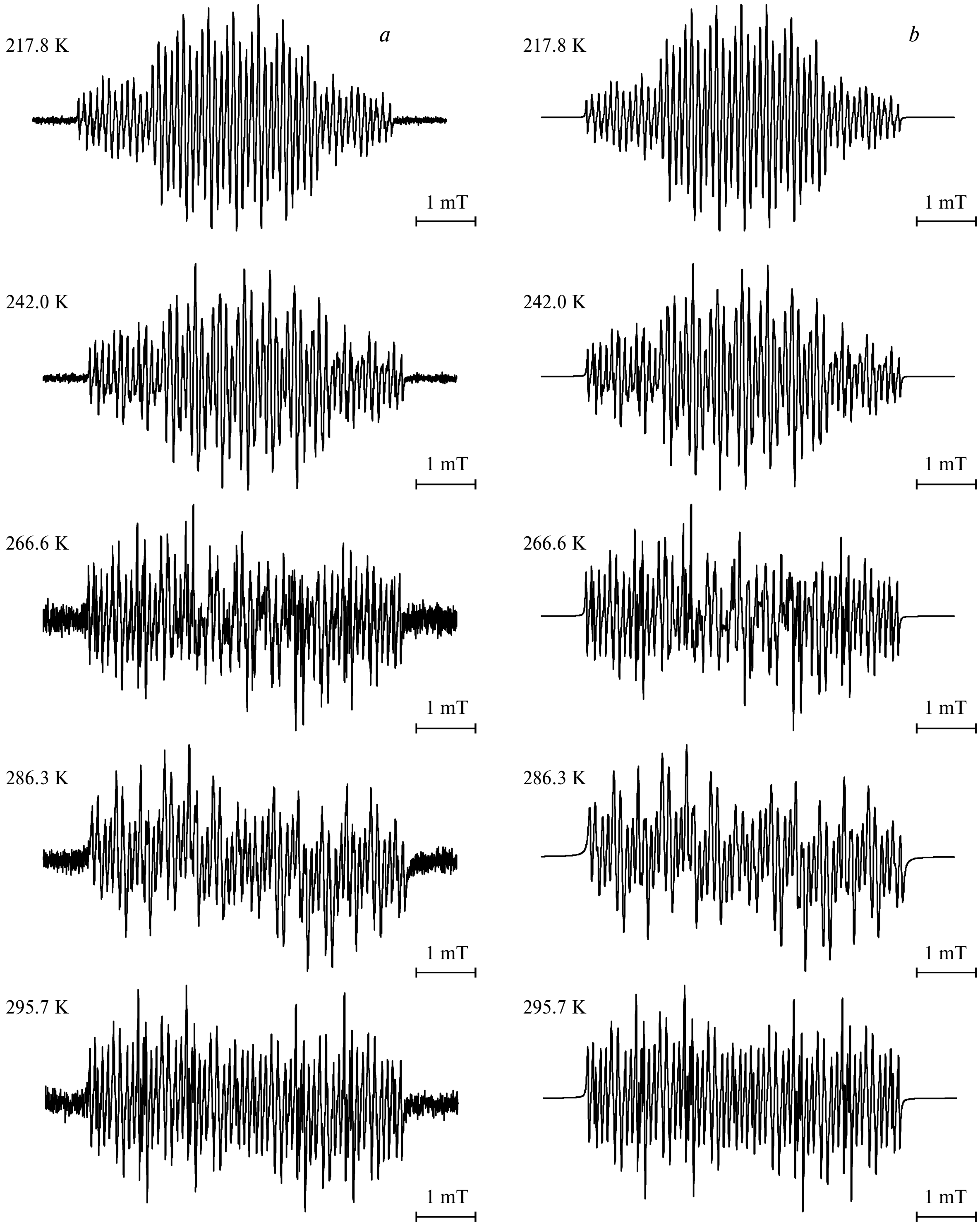

Fig. 1. Transformation of EPR spectrum of radical anion **1** in MeCN in the temperature interval 217.8—295.7 K: experimental data (*a*) and simulation (*b*).

The limit range of fast rotation of the CF_3 group is not attained in the temperature interval under study.

Provided that CF_3 group undergoes fast rotation the fluorine multiplet in the HFS should be a quartet with a binomial distribution of the spectral component intensities in a 1 : 3 : 3 : 1 ratio and averaged HFC constant value ($<a_F>$) equal to one third of the fluorine multiplet extension (Δ_F), that is, $<a_F> = 1/3\Delta_F$. The Δ_F value and

Table 1. Simulated HFC constants (a_i/mT) in EPR spectra of radical anion **1** in MeCN at different temperatures

T/K	$a_{F(1)}$	$a_{F(2)}$	$a_{F(3)}$	a_N	$a_{H(4)}$	$a_{H(6)}$	$a_{H(5)}$	$a_{H(3)}$
217.8	1.2687	1.2653	0.1121	0.8414	0.4182	0.3185	0.1259	0.0918
222.3	1.2691	1.2667	0.1140	0.8390	0.4184	0.3180	0.1262	0.0915
227.2	1.2696	1.2666	0.1156	0.8372	0.4185	0.3175	0.1265	0.0914
227.7	1.2663	1.2607	0.1129	0.8450	0.4161	0.3181	0.1260	0.0920
232.6	1.2704	1.2668	0.1172	0.8356	0.4186	0.3171	0.1268	0.0913
237.0	1.2708	1.2664	0.1189	0.8339	0.4187	0.3165	0.1273	0.0912
242.0	1.2715	1.2661	0.1205	0.8324	0.4188	0.3160	0.1276	0.0911
246.9	1.2721	1.2656	0.1228	0.8309	0.4189	0.3154	0.1276	0.0909
252.1	1.2727	1.2647	0.1249	0.8297	0.4191	0.3148	0.1278	0.0908
256.8	1.2720	1.2646	0.1271	0.8283	0.4190	0.3143	0.1279	0.0906
261.7	1.2697	1.2659	0.1294	0.8273	0.4191	0.3139	0.1280	0.0905
266.6	1.2717	1.2634	0.1335	0.8249	0.4192	0.3131	0.1284	0.0900
271.6	1.2687	1.2627	0.1360	0.8249	0.4192	0.3126	0.1284	0.0901
276.5	1.2679	1.2595	0.1406	0.8239	0.4192	0.3122	0.1287	0.0898
281.4	1.2673	1.2554	0.1460	0.8231	0.4193	0.3119	0.1291	0.0898
286.3	1.2583	1.2491	0.1617	0.8219	0.4193	0.3114	0.1296	0.0894
291.3	1.2434	1.2520	0.1748	0.8212	0.4194	0.3120	0.1295	0.0895
291.3*	1.2329	1.2574	0.1791	0.8211	0.4194	0.3108	0.1298	0.0888
295.7	1.2513	1.2348	0.1872	0.8201	0.4196	0.3105	0.1298	0.0895

* Obtained upon rapid increase in temperature from 217.8 K in order to check the reproducibility of the experimental results.

the overall HFS extension (Δ_{HFS}) vary only slightly, but monotonically. In the temperature interval 217—296 K they can be approximated by a quadratic function

$$\Delta = A + B \cdot T + C \cdot T^2. \quad (1)$$

The approximation parameters and correlation coefficients r (Δ_F, Δ_{HFS}, and A values are given in mT, B is given in mT K^{-1}, and C is given in mT K^{-2}) are listed below.

Parameter	A	B	−C	r^2
Fluorine multiplet	2.3001	0.002501	$4.232 \cdot 10^{-6}$	0.9056
Overall HFS	5.2833	0.001155	$2.327 \cdot 10^{-6}$	0.9220

The EPR spectral model used in this work corresponds to a general pattern of the HFS formed by multiplets originating from independent nuclei:

$$2F(1)_{CF_3} \times 2F(2)_{CF_3} \times 2F(3)_{CF_3} \times 3N \times 2H(4) \times 2H(6) \times$$
$$\times 2H(5) \times 2H(3).$$

The smallest HFC constant was obtained for proton in position 3 (Table 1). Parameters were optimized by minimizing the sum of the squared differences between ordinates in the numerical arrays of the model and experimental EPR spectra

$$D = \Sigma_i[\Delta Y_i]^2/\Sigma_i Y_i^2 \to \min. \quad (2)$$

The values of the optimization criterion D are listed in Table 2.

The HFS model takes into account two relaxation mechanisms, namely, dipolar broadening (d) of the components of the nitrogen triplet and exchange broadening (e) of the components of the fluorine multiplet.

Near the lower boundary of the temperature interval studied in this work (217.8—237 K) the HFS has a triplet pattern (Fig. 2), the spectral component intensity ratio of the low-temperature fluorine multiplet is very similar to the binomial ratio (T = 217.8 K), and optimization leads to nearly equal values of the constants of HFC with two of three ^{19}F nuclei. They differ only slightly, which is an indication of small-amplitude torsional motions near the equilibrium conformation of radical anion **1**. In the equilibrium conformation, the constants should become equal,

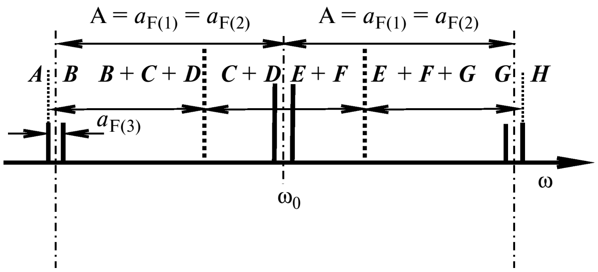

Fig. 2. Schematic pattern of fluorine multiplet in the HFS of the EPR spectrum of radical anion **1** in MeCN for the limiting cases of slow and fast motions ($a_{F(1)} = a_{F(2)} = A$; 217 K < T < 237 K). Degenerate components of the fluorine quartet in the limiting case of fast motion are denoted by dashed lines.

Table 2. Simulated contributions to the linewidth in the EPR spectrum of radical anion **1** in MeCN (W_0, $W_{N(+1)}$, and $W_{N(-1)}$), spectral density ($j_F(m_i)$), correlation time of hindered rotation of CF_3 group (τ_F), and values of the optimization criterion (D)

T/K	W_0	$W_{N(+1)} \cdot 10^4$	$W_{N(-1)} \cdot 10^3$	$j_F(m_i) \cdot 10^3$	$\tau_F \cdot 10^8$ /s rad^{-1}	$D \cdot 10^2$
	mT					
217.8	0.01403	9.730	2.4508	0.3705	1533.5	0.6895
222.3	0.01416	3.799	2.5146	0.6980	814.0	0.6512
227.2	0.01434	0.647	2.2199	1.1634	488.4	0.5867
227.7	0.02074	3.654	3.1643	1.8202	312.1	0.5706
232.6	0.01460	−2.350	2.0826	1.8648	304.7	0.6286
237.0	0.01509	−3.850	1.9273	2.7699	205.1	0.6043
242.0	0.01576	−4.530	1.8311	4.0663	139.7	0.633
246.9	0.01634	−4.640	1.6698	6.2081	91.5	0.7497
252.1	0.01708	−4.170	1.4635	8.6440	65.7	0.8666
256.8	0.01827	−5.810	1.2106	12.2494	46.4	1.1025
261.7	0.01957	−5.050	0.9551	16.7216	34.0	1.2582
266.6	0.01651	−2.390	0.7874	20.1374	28.2	6.5061
271.6	0.02337	−4.190	0.8341	30.0634	18.9	1.9077
276.5	0.02592	−2.130	0.8858	39.4455	14.4	2.0785
281.4	0.02839	−1.610	0.9402	48.8775	11.6	2.8993
286.3	0.03288	−2.390	1.0300	62.0847	9.2	3.9287
291.3	0.02824	−2.970	0.6833	75.5765	7.5	2.4257
291.3*	0.03470	−0.730	0.7038	65.9581	8.6	3.5817
295.7	0.01955	1.726	0.3330	75.8783	7.5	4.0424

* Obtained upon rapid increase in temperature from 217.8 K in order to check the reproducibility of the experimental results.

i.e., $a_{F(1)} = a_{F(2)} = A$. This means that the equilibrium conformation of radical anion **1** has C_s symmetry (two atoms, F(1) and F(2), of the CF_3 group are equivalent and equidistant from the benzene ring plane in which the third fluorine nucleus and other atomic nuclei lie). The constant of hyperfine coupling with the third ^{19}F nucleus is an order of magnitude smaller, *i.e.*, $a_{F(3)} = a \ll A$ (see Fig. 2) and increases with temperature.

Uniformly determined dihedral angles[8] between the C—C—F plane and the plane in which the axis of the p_π-AO of the neighboring π-radical center (arene carbon atom) lies are 30, 150, and 270°.

The values of the fluorine HFC constants of the low-temperature fluorine multiplet (see Table 1) are in good agreement with the corresponding values calculated using the theory of angular functions of the β-fluorine HFC.[8]

The amplitude ratio of the outermost HFS components, Y_{+1}/Y_{-1}, equals 1.27. Therefore, the broadenings of the nitrogen triplet components corresponding to $m_N = \pm 1$ differ by at most 12—13% and the dynamics of Brownian reorientations near the lower boundary of the temperature range studied corresponds to the case of fast rotation.[9]

The high-temperature region (270—296 K) is characterized by very fast rotational diffusion of radical anion **1**, complete averaging of the anisotropic HFC, and the lack of line broadening in the nitrogen triplet.

Because the width fluctuations of the nitrogen components of the HFS are similar to their absolute values, it is impossible to determine the activation parameters of rotational diffusion. As the temperature increases, six central components of the fluorine multiplet are broadened. Their shifts are very small and therefore we can extrapolate the EPR spectrum to the neighboring region of slow motion using the quasi-static model. Because of this, the model HFS is represented by a superposition of Lorentzian lines and includes the dynamic perturbations (*d* and *e*) in the form of contributions to the widths of the corresponding components.

The first derivative of a normalized Lorentzian component of the HFS is given by

$$Y'(x) = -(2\Gamma/\pi) \cdot (x - x_0)/[\Gamma^2 + (x - x_0)^2]^2, \qquad (3)$$

where x_0 and Γ are the coordinate of the center of the line on the abscissa axis and the line half-width at half-height, respectively.

The HFC constants are represented by the following array:

$$a_n \in H;$$
$$H = (a_{F(1)}; a_{F(2)}; a_{F(3)}; a_N; a_{H(4)}; a_{H(6)}; a_{H(5)}; a_{H(3)}). \qquad (4)$$

The nuclear spins I_n are equal to 1 (^{14}N) and 1/2 (^1H, ^{19}F) and their projections are $m_N \in (-1, 0, +1)$ and

$m_{n\neq\mathrm{N}} \in (-1/2, +1/2)$. The nuclei that give rise to HFS (^{19}F(1); ^{19}F(2); ^{19}F(3); ^{14}N; ^{1}H(4); ^{1}H(6); ^{1}H(5); ^{1}H(3)) are denoted by the subscript "n" ($1 < n < 8$). Quantum numbers of the nuclear spin projections form the arrays M_k that enumerate the HFS components ($k_{\mathrm{max}} = \Pi_n(2I_n + 1) = 3\cdot 2^7 = 384$, $1 \le k \le k_{\mathrm{max}}$)

$$m_{kn} \in M_k;$$
$$M_k = (m_{\mathrm{F(1)}};\ m_{\mathrm{F(2)}};\ m_{\mathrm{F(3)}};\ m_{\mathrm{N}};\ m_{\mathrm{H(4)}};\ m_{\mathrm{H(6)}};\ m_{\mathrm{H(5)}};\ m_{\mathrm{H(3)}})_k. \quad (5)$$

Positions of the HFS components relative to the center of the HFS are given by

$$\begin{aligned} x_{0k} &= x_0(m_{\mathrm{F(1)}};\ m_{\mathrm{F(2)}};\ m_{\mathrm{F(3)}};\ m_{\mathrm{N}};\ m_{\mathrm{H(4)}};\ m_{\mathrm{H(6)}};\ m_{\mathrm{H(5)}};\ m_{\mathrm{H(3)}})_k = \\ &= (H : M_k) = \Sigma_n a_n m_{kn} = m_{\mathrm{F(1)}}a_{\mathrm{F(1)}} + m_{\mathrm{F(2)}}a_{\mathrm{F(2)}} + \\ &+ m_{\mathrm{F(3)}}a_{\mathrm{F(3)}} + m_{\mathrm{N}}a_{\mathrm{N}} + m_{\mathrm{H(4)}}a_{\mathrm{H(4)}} + m_{\mathrm{H(6)}}a_{\mathrm{H(6)}} + \\ &+ m_{\mathrm{H(5)}}a_{\mathrm{H(5)}} + m_{\mathrm{H(3)}}a_{\mathrm{H(3)}}. \end{aligned} \quad (6)$$

The model for the shape of the HFS with the normalization constant *Amp*, which sets the scale of the ordinate axis, has the form

$$Y'(x) = -Amp\cdot\Sigma_k\{\Gamma_k\cdot(x - x_{0k})/[\Gamma_k^2 + (x - x_{0k})^2]^2\}. \quad (7)$$

The half-width of the kth Lorentzian component of the HFS (Γ_k) is defined as the sum of three contributions, being the key source of information on the dynamics in radical anion **1**

$$\begin{aligned} \Gamma(m_{\mathrm{N}};\ m_{\mathrm{F(1)}};\ m_{\mathrm{F(2)}};\ m_{\mathrm{F(3)}}) &= W_0 + W_{\mathrm{N}}(m_{\mathrm{N}}) + \\ &+ W_{\mathrm{F}}(m_{\mathrm{F(1)}};\ m_{\mathrm{F(2)}};\ m_{\mathrm{F(3)}}), \end{aligned} \quad (8)$$

where $W_{\mathrm{N}}(m_{\mathrm{N}})$ is the contribution associated with modulation of the anisotropic HFC with the ^{14}N nucleus by rotational diffusion of radical anion **1**; $W_{\mathrm{F}}(m_{\mathrm{F(1)}};\ m_{\mathrm{F(2)}};\ m_{\mathrm{F(3)}})$ is the relaxation contribution caused by modulation of the isotropic HFC with ^{19}F nuclei in the CF$_3$ group; and W_0 is the contribution including all other spin relaxaton channels not related to the broadenings mentioned above.

Rotation of the CF$_3$ group causes no spin density fluctuations in the benzene ring, and the character of rotational diffusion in the whole temperature interval is similar to very fast. The relaxation contributions to the nitrogen triplet linewidths (W_{N}) in the whole temperature range are small and exhibit a large scatter. They can be described as usually[10]

$$W_{\mathrm{N}}(m_{\mathrm{N}}) = A_0 + (A + B\cdot m_{\mathrm{N}} + C\cdot m_{\mathrm{N}}^2)\tau_{\mathrm{c}}, \quad (9)$$

where A, B, and C are the electron spin parameters of the radical anion and τ_{c} is the correlation time of rotational diffusion. The parameters in Eq. (9) are calculated using the sum and difference between small values $W_{\mathrm{N}(\pm 1)}$, but they do not provide a sufficient accuracy in the determination of the activation parameters of rotational diffusion, that is, activation energy (E_{c}^*) and correlation time ($\tau_{\mathrm{c}} = \tau_{\infty,\mathrm{c}}\cdot\exp(E_{\mathrm{c}}^*/T)$)

$$W_{\mathrm{N}-} = [W_{\mathrm{N}(1)} - W_{\mathrm{N}(-1)}]/2 = B\cdot\tau_{\mathrm{c}}, \quad (10)$$

$$W_{\mathrm{N}+} = [W_{\mathrm{N}(+1)} + W_{\mathrm{N}(-1)}]/2 = A_0 + (A + C)\tau_{\mathrm{c}}. \quad (11)$$

Nevertheless, there is a linear portion of the logarithmic anamorphosis $\ln B(T^{-1})$ in a narrow temperature interval 242 K $\le T \le$ 276 K, which makes it possible to perform a formally correct estimation of E_{c}^* at about 11.5 kJ mol^{-1}.

Near the upper boundary of the temperature interval studied in this work the amplitudes of the outermost components of the HFS are equal and $W_{\mathrm{N}}(|m_{\mathrm{N}}|) \approx 0$. Therefore, one has

$$W_{\mathrm{F}}(m_{\mathrm{F(1)}},\ m_{\mathrm{F(2)}},\ m_{\mathrm{F(3)}}) = W_{\mathrm{F}}(-m_{\mathrm{F(1)}},\ -m_{\mathrm{F(2)}},\ -m_{\mathrm{F(3)}}).$$

Now we will show how they can be expressed through the spectral density j_{F}.

The complex spectral density $J(\omega) = j(\omega) - ik(\omega)$ at the angular frequency ω is the Fourier transformation of the correlation function of a process characterized by the correlation time τ, where $(\omega\tau)j(\omega) = k(\omega)$.[10] If two transitions, l and m, are characterized by similar frequencies that are modulated by the same stochastic process ($\omega_l \approx \omega_m \approx \omega_0$, $|\Delta_{lm}\omega| \ll \omega_0$) with a common correlation time τ, the ratios of the shifts and the broadenings of the spectral components are equal because one has

$$|k_l(\omega)/k_m(\omega)| = |j_l(\omega)/j_m(\omega)|. \quad (12)$$

Transformation of the fluorine octet (lines ***A***, ***B***, ***C***, ***D***, ***E***, ***F***, ***G***, and ***H***) in the HFS of the EPR spectrum of radical anion **1** in MeCN is due to the fact that static situation (equilibrium orientation of the CF$_3$ group) is changed by slow (SE) and then fast (FE) rotation of this group

$$\begin{aligned} &\boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C}, \boldsymbol{D}, \boldsymbol{E}, \boldsymbol{F}, \boldsymbol{G}, \boldsymbol{H} \xrightarrow{\mathrm{SE}} \\ &\longrightarrow \boldsymbol{A}, \boldsymbol{B}, (\boldsymbol{C} + \boldsymbol{D}), (\boldsymbol{E} + \boldsymbol{F}), \boldsymbol{G}, \boldsymbol{H} \xrightarrow{\mathrm{FE}} \\ &\longrightarrow \boldsymbol{A}, (\boldsymbol{B} + \boldsymbol{C} + \boldsymbol{D}), (\boldsymbol{E} + \boldsymbol{F} + \boldsymbol{G}), \boldsymbol{H}. \end{aligned}$$

In the former case (SE) the lines (***E*** + ***F***) and (***C*** + ***D***) are shifted by ±(1/2)a and the lines ***G*** and ***B*** are shifted by (±1)[A – (1/2)a] with respect to the center. In the latter case (FE) the lines (***E*** + ***F*** + ***G***) and (***B*** + ***C*** + ***D***) are shifted by $\pm(1/2)\langle a_{\mathrm{F}}\rangle$ from the center. If the character of the motion changes (SE → FE), the components ***G*** and ***B*** are shifted by $\delta' = |\pm(2/3)(\mathrm{A} - a)|$ and the lines (***E*** + ***F***) and (***C*** + ***D***) are shifted by $\delta'' = |\pm(1/3)(\mathrm{A} - a)|$ (see Fig. 2). Thus, the ratio $\delta'/\delta'' = 2$, but the outermost lines ***A*** and ***H*** retain their positions and widths. As a result, both the line shifts and line broadenings under slow exchange (SE) are related by a proportion 0 : 2 : 1 : 1 : 1 : 1 : 2 : 0 and the number of the optimized HFS parameters is minimum (HFC constants, contributions W_0, $W_{N(+1)}$, $W_{N(-1)}$, and j_F; see Tables 1 and 2).

The line broadenings in the fluorine HFS are inversely proportional to the correlation time (τ_F)[10] and related to the spectral density j_F as follows

$$W_F(\boldsymbol{C}, \boldsymbol{D}, \boldsymbol{E}, \boldsymbol{F}) = 1/2 W_F(\boldsymbol{B}, \boldsymbol{G}) = \gamma_e^{-1}\tau_F^{-1} = j_F, \qquad (13)$$

where $\gamma_e = 1.76 \cdot 10^8$ rad s^{-1} mT^{-1} is the magnetogyric ratio of an electron.

In MeCN, the correlation time τ_F varies within a range of three orders of magnitude, namely, $7.5 \cdot 10^{-8}$ s rad^{-1} < < τ_F < $1.5 \cdot 10^{-5}$ s rad^{-1} (see Table 2). The Arrhenius activation equation in the theory of relaxation has the form:

$$\tau_F = \tau_{F,\infty} \cdot \exp(E_F^*/T). \qquad (14)$$

The linear dependence of $\ln\tau_F$ on the inverse temperature (Fig. 3) has a very high correlation coefficient ($r^2 = 0.9978$). The pre-exponent ($\tau_{F,\infty}$) and the activation energy (E_F^*) are $1.87 \cdot 10^{-14}$ s rad^{-1} and $3.654 \cdot 10^4$ J mol^{-1}, respectively.

The temperature dependences of the smallest HFC constant $a_{F(3)}$ and the arithmetic mean of two other HFC constants, $a_{F(0)} = (a_{F(1)} + a_{F(2)})/2$, can be approximated as follows:

$$a_{F(i)}(T) = S_{F(i)}\exp(-K_{F(i)}/T) + Q_{F(i)}/T + P_{F(i)} \qquad (15)$$

($i = 0, 3$). The coefficients of expression (15) are listed in Table 3. Two curves, $a_{F(0)}(T)$ and $a_{F(3)}(T)$, intersect at a point ($T^* = 338.8$ K, $a_F^* = 0.8474$ mT) corresponding to the onset of fast exchange (see Fig. 3).

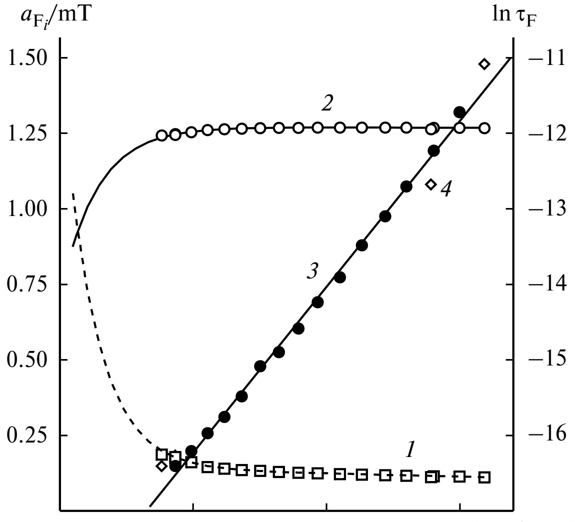

Fig. 3. HFC constants $a_{F(3)}$ (*1*) and $a_{F(0)}$ (*2*) and $\ln\tau_F$ values (*3*) plotted *vs.* inverse temperature. Points excluded from linear dependence (*3*) are denoted (*4*). Curves (*1*) and (*2*) are extrapolated to the point of the onset of fast rotation of CF_3 group.

Table 3. Coefficients in Eq. (15) used for approximation of temperature dependences of isotropic HFC constants with ^{19}F nuclei

Coefficient	$a_{F(i)}$/mT	
	$(a_{F(1)} + a_{F(2)})/2$	$a_{F(3)}$
$S_{F(i)}$/mT	$-1.121 \cdot 10^7$	$2.242 \cdot 10^7$
$K_{F(i)}$/K	5785.86	5850.42
$Q_{F(i)}$/mT K^{-1}	−5.4191	−16.628
$P_{F(i)}$/mT	1.2919	0.1882
r^2	0.9904	0.9923

We performed a simple statistics-based derivation of the function (15) using a model of intramolecular torsional trigonal rotor (CF_3 group).[11] For brevity, we do not present it here. Mention may only be made that it requires the use of the angular dependences of the β-fluorine HFC[8] in explicit form and does not require both an exact spectrum of energy levels and explicit form of the rotor potential. Theory predicts that two functions, $a_{F(3)}(T)$ and $a_{F(0)}(T)$, have the same exponents $K_{F(3)} = K_{F(0)} = K$ and their pre-exponents differ by a factor of two and have different signs, namely, $2S_{F(3)} = -S_{F(0)}$. Our independent numerical optimization of the parameters of both curves led to exactly the same results (see Table 3). The function (15) is a convenient palliative for the Boltzmann averaging of the stereospecific HFC constant over the energy levels of torsional trigonal rotor.

Two very similar HFC constants, $a_{F(1)}$ and $a_{F(2)}$, simulate the limiting values of a slowly fluctuating average HFC constant $a_{F(0)}$ under the conditions where the degenerate lines lose their Lorentzian shape, being split into Lorentzian components.

The HFC constant a_F^* at a hypothetical point of the onset of fast exchange is determined at the intersection point of the $a_{F(0)}(T)$ and $a_{F(3)}(T)$ plots using relation (15) and differs from the theoretical value by only 0.0399 mT, *i.e.*, $a_F^* = a_{F(0)}(T^*) = a_{F(3)}(T^*) \approx \langle a_F \rangle$. Taking into account the experimental conditions of EPR studies, this discrepancy is very small. At the same time the coincidence is evident, although we performed a long-range nonlinear extrapolation to the point that is distant from the region of EPR measurements.

Thus, in this work we experimentally studied and simulated the temperature dependence of the EPR spectrum of 2-trifluoromethylnitrobenzene radical anion in MeCN in the range 217—296 K and elucidated the dynamic reasons for the phenomenon. Near 217 K, radical anion **1** adopts the equilibrium conformation with C_s symmetry. As the temperature increases, slow hindered rotation of CF_3 group begins, but the limiting regime of fast rotation was not attained under the experimental conditions. Using numerical optimization, we determined the HFS parameters and the activation parameters of hindered rotation of the CF_3 group (key mechanism of the dynamic modulation of the HFS). The activation energy ($E_F{}^* = 36.5\pm0.5$ kJ mol^{-1}) is maximum for all Markoff internal motions in π-type free radicals studied to date.

References

1. E. G. Janzen and J. L. Gerlock, *J. Am. Chem. Soc.*, 1967, **89**, 4902.
2. J. W. Rogers and W. H. Watson, *J. Phys. Chem.*, 1968, **72**, 68.
3. E. A. Polenov, L. A. Shundrin, and D. V. Platonov, *Thesis of Repts Ampere 2000 — 30th Congress AMPERE of Magnetic Resonance and Related Phenomena (Lisbon, 23—28 July, 2000)*, Portugal, 2000, Proc., Ch. 6, 482.
4. A. K. Lyashchenko, T. A. Novskova, and V. A. Gaiduk, *J. Mol. Liq.*, 2001, **94**, 1.
5. A. K. Lyashchenko, A. S. Lileev, T. A. Novskova, and V. S. Kharkin, *J. Mol. Liq.*, 2001, **93**, 29.
6. P. P. Wiewiór, H. Shirota, and E. W. Castner, Jr., *J. Chem. Phys.*, 2002, **116**, 4643.
7. B. Kirchner and M. Reiher, *J. Am. Chem. Soc.*, 2002, **124**, 6206.
8. E. A. Polenov, K. V. Bozhenko, L. A. Shundrin, and D. M. Smekalkin, *Izv. Akad. Nauk. Ser. Fiz.*, 2004, **68**, 1066 [*Bull. Russ. Acad. Sci. Physics*, 2004, **68**, 1206 (Engl. Transl.)].
9. A. N. Kuznetsov, *Metod spinovogo zonda* [*The Spin Probe Method*], Nauka, Moscow, 1976, 47 pp. (in Russian).
10. G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139.
11. E. W. Stone and A. Maki, *J. Phys. Chem.*, 1962, **37**, 1326.

Received March 29, 2006;
in revised form June 19, 2006