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Spin-polarized EPR spectra of fullerene C_{60} dissolved in glassy ortho-terphenyl was measured in the temperature range of 80 – 240K. The temperature dependence of the spectra was successfully simulated using the model of fast pseudorotation of $^3C_{60}$ in a potential created by the surrounding solvent molecules. The strength of this potential was estimated at different temperatures. Near 240K this potential was found to decrease remarkably.

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Introduction

Since the discovery of fullerenes they attracted much attention because of unusual physical and chemical properties and because of possible technical application of fullerene-based materials. The fullerene C_{60} can be easily excited by visible light, which leads to the formation of triplet state of C_{60} with the quantum yield close to unity. This state is characterized by high electron spin polarization. That is why the fullerene-based materials can possibly be used as an active media for masers [1]. To create such materials it is necessary to investigate the dynamics of C_{60} in triplet state and its dependence on temperature, solvent and the time of delay after light flash.

Previously, the triplet state of C_{60} was studied by time-resolved EPR [2], OD EPR [3] and electron spin echo [4]. It was found that $^3C_{60}$ is characterized by non-zero ZFS parameters D and E, which slightly depends on the solvent. Also, the strong temperature dependence of spin-polarized EPR spectrum of $^3C_{60}$ was observed. However, so far the interpretation of this temperature dependence is not clear. In our opinion, the satisfactory numerical simulation of this dependence is lacking, and the convincing simulation was performed only for the case of very low temperatures (1.2 - 7K) [5], for which the dynamics of $^3C_{60}$ is probably frozen.

The aim of the present work is to study the $^3C_{60}$ dynamics at higher temperatures and to find the reasonable model explaining this dynamics, which would allow the adequate simulation of the temperature dependence of $^3C_{60}$ EPR spectrum.

Theory

The Triplet Energy Levels.

The hamiltonian of the molecule in triplet particles state consists of two main terms — Zeeman energy and energy of magnetic dipole-dipole interaction of two unpaired electron spins (H_D): $H = g\beta \boldsymbol{HS} + H_D$, where H is the magnetic field vector, $\boldsymbol{S}$ is triplet spin vector, $S = 1$, β is Borh magneton. For simplicity we assumed here the isotropic g-factor g. We can write H_D through the tensor D_{ij} of magnetic dipole-dipole interaction: $H_D = \frac{1}{2}S_iD_{ij}S_j$. In the framework of the principal axes of D_{ij} tensor (x, y, z) $\mathcal{H}_D = D\left(S_z^2 - \frac{1}{3}S^2\right) + E\left(S_x^2 - S_y^2\right)$, where D and E are zero-field splitting parameters.

In the same coordinate system the magnetic field vector may be written as $\boldsymbol{H} = H(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, where θ is polar and φ azimuthal angles of $\boldsymbol{H}$ vector, respectively. We can rewrite the H_D term in a framework of reference (X, Y, Z), which has Z axis parallel to magnetic field direction:

$$\mathcal{H}_D = \frac{1}{2}\left(D\left(\frac{1}{3}-\cos^2\theta\right) - E\sin^2\theta\cos 2\varphi\right)\left(\mathbf{S}^2 - 3S_Z^2\right). \cdot \tag{1}$$

We assume that $g\beta H >> D$, i.e. the high-field approximation is valid. The energy levels W_+, W_0 and W_- of high-field eigenstates T_+, T_0 and T_- are [6]:

$$W_+ = g\beta H + \frac{D}{2}\left(\cos^2\theta - \frac{1}{3}\right) + \frac{E}{2}\sin^2\theta\cos 2\varphi;\ \ W_0 = D\left(\frac{1}{3}-\cos^2\theta\right) - E\sin^2\theta\cos 2\varphi;$$

$$W_- = -g\beta H + \frac{D}{2}\left(\cos^2\theta - \frac{1}{3}\right) + \frac{E}{2}\sin^2\theta\cos 2\varphi. \tag{2}$$

The Spin Polarization of Triplet State.

The high-field triplet eigenfunctions T_+, T_0 and T_- can be rewritten trough zero-field eigenfunctions T_x, T_y and T_z as:

$$\begin{aligned} T_+ &= T_x\frac{i\sin\theta+\cos\theta\cos\varphi}{2} - T_y\frac{i\cos\varphi+\cos\theta\sin\varphi}{2} + T_z\frac{\sin\theta}{\sqrt{2}};\\ T_0 &= iT_x\sin\theta\sin\varphi + T_y\sin\theta\cos\varphi + T_z\cos\theta;\\ T_- &= -T_x\frac{i\sin\theta+\cos\theta\cos\varphi}{2} + T_y\frac{i\cos\varphi+\cos\theta\sin\varphi}{2} + T_z\frac{\sin\theta}{\sqrt{2}}. \end{aligned} \tag{3}$$

According to Eq. (3), the populations of high-field eigenstates p_+, p_0, p_- can be expressed via the populations of zero-field eigenstates p_x, p_y, p_{z}-:

$$p_0 = p_x\sin^2\theta\sin^2\varphi + p_y\sin^2\theta\cos^2\varphi + p_z\cos^2\theta.$$

$$p_+ = p_- = \frac{1}{2}p_x(\cos^2\theta\cos^2\varphi + \sin^2\varphi) + \frac{1}{2}p_y(\cos^2\theta\sin^2\varphi + \cos^2\varphi) + \frac{1}{2}p_z\sin^2\theta. \tag{4}$$

Therefore, the polarizations of allowed EPR transitions are:

$$p_+ - p_0 = p_- - p_0 = \frac{1}{2}p_x(\cos^2\theta\cos^2\varphi + \sin^2\varphi - 2\sin^2\theta\sin^2\varphi) +$$

$$+\frac{1}{2}p_y(\cos^2\theta\sin^2\varphi+\cos^2\varphi-2\sin^2\theta\cos^2\varphi)+\frac{1}{2}p_z(\sin^2\theta-2\cos^2\theta). \qquad (5)$$

Experiment

Fullerene C_{60} was dissolved in ortho-terphenyl at concentration of about 10^{-4}M. The solution was put in glass tube with a 4 mm inner diameter. Three freeze-pump-thaw cycles were executed, and then the tube was sealed under high vacuum. Before measurements the samples were quickly cooled in liquid nitrogen to obtain the glassy state of ortho-terphenyl.

Electron spin echo experiments were carried out on Bruker ESP-380E FT EPR spectrometer equipped with a dielectric cavity (Bruker ER 4118 X-MD-5) inside an Oxford Instruments CF 935 liquid cryostat. The temperature was controlled by cold nitrogen flow. For photoexcitation of the sample the pulses of second harmonic Nd-YAG laser Surelite I-10 were used with the wave-length 532 nm, pulse duration 10 ns, pulse energy 20 mJ and the pulse repetition rate 5 Hz. The microwave pulse sequence $\pi/2 - \tau - \pi - \tau -$ *echo* with $\tau = 120$ ns was used. The whole echo signal in time domain was integrated by a built-up integrator. The delay after laser flash was about 100 ns. The microwave frequency was 9.493 GHz.

Results and discussion.

The echo detected EPR spectra were observed at different temperatures at the range of 80 – 240 K. They are shown in Fig.1. The spectra are spin-polarized with a low-field absorptive part and high-field emissive part. In Fig. 1 one can see progressive narrowing of the spectrum with temperature increase.

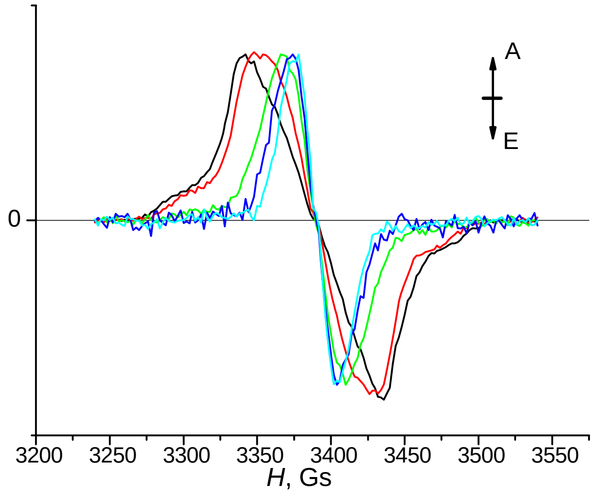

Fig.1. Echo-detected EPR spectra of the triplet state of C_{60} in ortho-terphenyl at different temperatures. The spectra are normalized at the absorptive maximum.

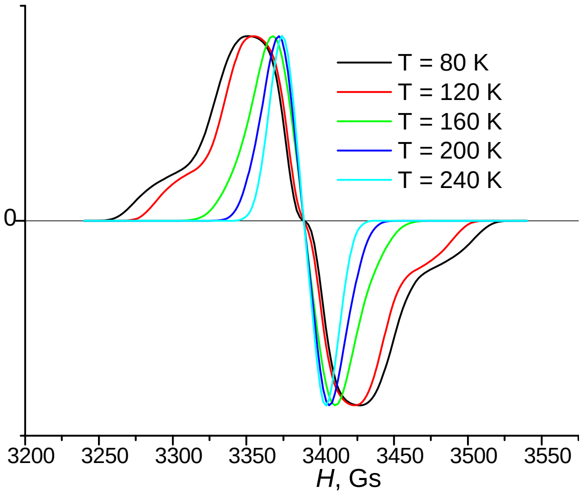

Fig.2. Simulations of ED EPR spectra (see Fig. 1) using the model of $^3C_{60}$ fast pseudorotation in potential $U = -V\cos\alpha$ (see text).

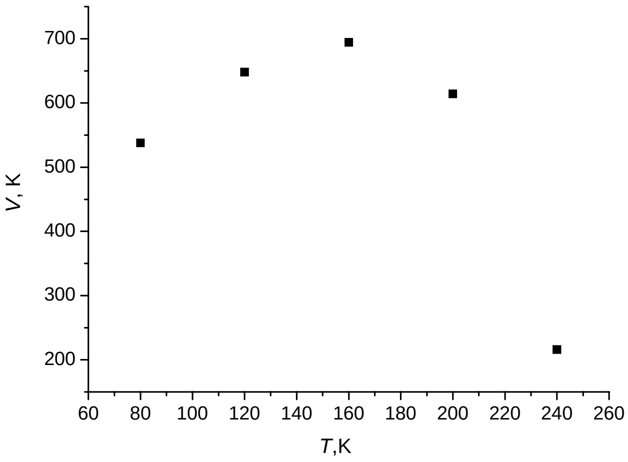

Fig.3. Temperature dependence of the strength of the potential V (see Eq. 6), obtained from the simulation of $^3C_{60}$ EPR spectra.

For explaining this phenomenon the model of fullerene fast pseudorotation (dynamic Jahn-Teller effect) in a potential $U = -V\cos\alpha$ [7] was suggested. Here α is the angle within a range of $[0,\pi]$ between the z-axis of tensor D_{ij} and the direction determined by local surrounding of C_{60} molecule. Previously, the model of pseudorotation was used for explaining the temperature change of $^3C_{60}$ EPR spectrum in the range of 4 – 80K [4].

We have simulated the obtained spectra numerically in MATLAB program package in the following way. The total spectrum was obtained by the powder average of the $T_0 \to T_+$ and $T_0 \to T_-$ transitions of the individual triplets, which are characterized by the angles θ and φ. The polarization of the spin transitions was calculated according to Eq. (5). The frequencies of the transitions were calculated according to Eq. (2), and the averaging of these frequencies over the α angle was performed. The probability distribution $W(\alpha)$ was derived from Boltzmann law:

$$\frac{dW}{d\alpha} = \exp\left(-\frac{V\cos\alpha}{kT}\right)\cdot\sin\alpha \ . \tag{6}$$

During the simulation we kept fixed the parameters D = 110G, E = 3G, g = 2.0002, $p_x = p_y = 0$, $p_z = 1$. The only fitting parameter was the strength of the potential V. The simulated spectra are shown on Fig. 2. Very good agreement between the experimental and the simulated spectra can be noticed. The averaging over α leads to partial averaging of the zero-field splitting, which in turn results in narrowing of the simulated spectra.

The dependence of the obtained V values on the temperature is presented on Fig. 3. In the range 80 – 200K it is nearly temperature-independent with the mean value V ≈ 600K. The severe decrease of V is observed at 240K. This is probably caused by the increasing of the molecular mobility of ortho-terphenyl at higher temperature, which facilitates the pseudorotation of $^3C_{60}$. Note that near 240K in ortho-terphenyl a so-called dynamical transition is observed that is characterized by the onset of large-amplitude stochastic motion [8].

To estimate the rate of the $^3C_{60}$ pseudorotation we measured the transverse relaxation time T_2 of $^3C_{60}$. For all temperatures it was found that T_2 > 200 ns, and the decrease of T_2 with temperature increase was observed. At higher temperatures, when the EPR spectrum distortion is substantial, the scale of the frequency change due to pseudorotation $\Delta\omega$ is in order of D = 110G ≈ 2000 MHz. For the fast motion the contribution of the pseudorotation to transverse relaxation rate $1/T_2$ can be calculated according to the Redfield theory:

$$1/T_2 = \tau_c <\Delta\omega^2>, \tag{7}$$

where τ_c is the correlation time of the pseudorotation, and $<\Delta\omega^2>$ is the mean-square value of the fluctuation of the resonance frequency. From the Eq. (7) we can estimate $\tau_c \leq 10^{-12}$ s, which is in agreement with previous estimations [9].

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References

1. Blank A., Kastner R., Lebanon H. *IEEE Trans. Microwave Theory Tech.* **46,** 2137(1998).
2. Wasilewski M.R., O’Neil M.P., Lykke K.R., Pellin M.J., and Gruen D.M. *J. Am. Chem. Soc.* **113**, 2774 (1991).
3. Lane P.A., Swanson L.S. *Phys. Rev. Lett.* **68,** 887 (1992).
4. Benatti M., Grupp A., and Mehring M. *J. Chem. Phys.* **102**, 9457 (1995).
5. R. Dauw X.L., van den Berg G.J.B., van den Heuvel D.J., Poluektov O. G., and Groenen E.J.J. *J. Chem. Phys.* **112**, 7102 (2000).
6. Seidel H., Mehring M., and Stehlik D. *Chem. Phys. Lett.* **104**, 552 (1984).
7. de Groot M.S., Hesselmann I.A.M., and van der Waals J.H. *Molecular Physics* **16**, 45 (1969).
8. Dzuba S.A., Kirilina E.P., Salnikov E.S. *J. Chem. Phys.* **125**, 054502 (2006).
9. Closs G.L., Gautam P., Zhang P., Krusic P.J., Hill S.A., Wasserman E.J. *J. Phys. Chem.* **96**, 5228 (1992).

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