Spin relaxation of fullerene C_{70} photoexcited triplet in molecular glasses: Evidence for onset of fast orientational motions of molecules in the matrix near 100 K

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Electron spin echo (ESE) was applied to study transversal spin relaxation of photoexcited triplet state of fullerene C_{70} molecules in glassy *o*-terphenyl and *cis-/trans*-decalin matrices (glass transition temperatures of 243 and 137 K, respectively). The relaxation rate T_2^{-1} was found to increase sharply above 110 K in *o*-terphenyl and above 100 K in decalin. It is suggested that this increase arises from interaction of $^3C_{70}$ pseudorotation with fast molecular librations in the matrix. Both these types of motion involve atomic vibrations and are uniaxial in their nature, the known literature data on Raman light scattering and others indicate that molecular librations may be thermally activated in glasses just near 100 K. The increase in T_2^{-1} near 100 K is not observed for photoexcited triplet state of fullerene C_{60}, for which pseudorotation is not uniaxial. As the fullerene molecule has a size much larger than that for glass solvent molecules, it is likely that molecular librations in the matrix are of collective nature. © *2009 American Institute of Physics*. [doi:10.1063/1.3244983]

I. INTRODUCTION

Disordered materials share a number of universal phenomena related to molecular motions. For vibrational motions, a so-called dynamical transition is known. It appears in molecular glasses, in proteins, and in other biomolecules as an abrupt deviation of the structural mean square displacement $\langle r^2 \rangle$ from a linear temperature dependence. Below the dynamical transition temperature T_d atomic motions may be described as harmonic oscillations. Above T_d motion is anharmonic or diffusive (or stochastic). It is observed for molecular glasses,[1–6] proteins,[7–15] membranes,[16,17] and other biomolecules[18] by neutron scattering and Mössbauer absorption and manifests itself in molecular dynamics simulations. For proteins T_d lies between 180 and 230 K, and it is believed to affect their physiological function.[13,15,16] For simple molecular glass formers T_d is normally close to glass transition temperature T_g.

Also, an additional dynamical transition in the vicinity of 100 K was found in biological systems.[13,18–21] In most cases it is ascribed to methyl group rotation which becomes active in the time window of the experiment. Also, a partial onset of diffusive protein motion was proposed to occur near 100 K.[19]

Recently, electron spin echo (ESE) of photoexcited triplet state of fullerene C_{60} molecules in *o*-terphenyl, 1-methylnaphthalene, and decalin glassy matrices was studied.[22] A sharp increase in the transversal spin relaxation rate T_2^{-1} temperature dependence was found near 240 K for *o*-terphenyl

and near 100 K for two other glasses. It was assigned to the influence of the dynamical transition in the glass[1–18] on pseudorotation of $^3C_{60}$ molecule.

In this work we study $^3C_{70}$ photoexcited triplet state in *o*-terphenyl and *cis-/trans*-decalin glasses (glass transition temperatures T_g are 243 and 137 K, respectively). $^3C_{70}$ is known to experience pseudorotation along the axis of fivefold symmetry.[23–26] We show that spin relaxation of $^3C_{70}$ also manifests an abrupt increase with temperature. However, in *o*-terphenyl glass this increase occurs at temperatures near 110 K that is remarkably lower than that found for $^3C_{60}$ fullerene.[22] In the case of decalin glass the increase is observed near 100 K and it is remarkably sharper than that for $^3C_{60}$ in this glass. These differences in $^3C_{70}$ and $^3C_{60}$ behavior may drive to some conclusions on the nature of molecular motions in disordered materials.

II. EXPERIMENT

Fullerene C_{70} (Aldrich, 99% purity) was dissolved either in *o*-terphenyl (Tokyo, Kasei) or in decalin (1:1 mixture of *cis-* and *trans*-decalin, Sigma-Aldrich), at concentration of about $5 \times 10^{-4}M$. The solutions were put in glass tubes of a 5 mm outer diameter. Three freeze-pump-thaw cycles were executed and then tubes were sealed under vacuum. Prior the measurements the *o*-terphenyl sample was heated up to a melting point and then it was quickly frozen in liquid nitrogen to obtain a glassy state. In all cases frozen samples presented themselves a transparent glass.

ESE experiments were carried out on an *X*-band Bruker ESP-380E FT EPR spectrometer equipped with a dielectric cavity (Bruker ER 4118 X-MD-5) inside an Oxford Instruments CF 935 cryostat. A two-pulse microwave pulse sequence $\pi/2 - \tau - \pi - \tau -$echo was used. The pulse durations

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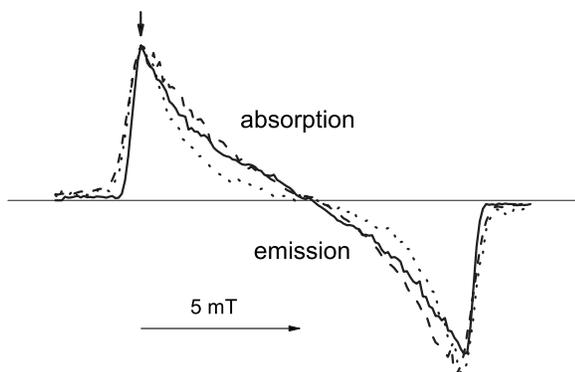
FIG. 1. ED EPR spectra of the $^3C_{70}$ photoexcited triplet state taken at 100 ns DAF and 120 ns delay τ between two microwave pulses. Spectra are normalized to the same maximal amplitude. Thin horizontal line demarks the zero level of the signal, the positive intensity means absorption, and the negative one means emission. Dashed line: o-terphenyl, 85 K. Solid line: decalin, 80 K. Dotted line: o-terphenyl, 110 K. The arrow shows the magnetic field position where the signal decays were measured (data in Figs. 2 and 3).

FIG. 2. A semilogarithmic plot of the echo decay with the τ delay increase and magnetic field fixed at the position shown by arrow in Fig. 1. The curves are shifted arbitrarily along the vertical axis. (a) o-terphenyl, 85 K. (b) decalin, 83 K. (c) o-terphenyl, 105 K. Dashed lines: linear approximation of the initial decays. The slope of these lines determines the transversal relaxation rates T_2^{-1}.

were 16 and 32 ns for the $\pi/2$ and π pulses, respectively. The spectrometer dead time was about 100 ns. The echo signal in the time domain was integrated on a built-in spectrometer integrator.

For sample photoexcitation the second harmonic of a pulsed neodymium-doped yttrium aluminum garnet laser Surelite I-10 was used, with the wavelength of 532 nm, the pulse duration of 10 ns, the pulse energy of 5 mJ, and the pulse repetition rate of 10 Hz. Temperature was controlled by a cold nitrogen flow and measured with a copper-constantan thermocouple attached to the sample. The minimal delay after flash (DAF) for the first microwave pulse was about 100 ns.

III. RESULTS

Echo signal taken when magnetic field is scanned with the all time delays fixed results in a so-called echo-detected (ED) EPR spectrum. Figure 1 shows ED EPR spectra for $^3C_{70}$ at some selected temperatures. These spectra look similar to the time-resolved EPR spectra reported previously for approximately the same temperatures.[23–25] Spectra in Fig. 1 are spin polarized, with the low-field absorptive part and the high-field emissive one. Spectra are normalized to the same maximal intensity. One can see that lineshape in Fig. 1 only slightly depends on the matrix and on temperature.

The C_{70} molecule in the ground state belongs to D_{5h} symmetry. The Z molecular axis normally is assigned to the axis along which the molecule is elongated. The two perpendicular axes, X and Y, lie in the equatorial plane. After photoexcitation into triplet $^3C_{70}$ state the symmetry is lowered to the C_{2v} type because of Jahn–Teller distortion, with lengths of the molecular bonds changing by ~ 0.01 Å.[27] These distortions due to the dynamical nature of the Jahn–Teller effect are hopping from bond to bond. This hopping is called pseudorotation. The concept of pseudorotation was attracted to explain EPR lineshape of $^3C_{70}$ in a number of previous studies,[23–26] where it was described in detail. Pseudorotation formally may be considered as hopping of the X and Y axes

between five equivalent sites.[23] It results in anisotropy of spin-lattice relaxation, which is the slowest for the magnetic field orientation along the Z molecular axis. This anisotropy determines the experimental ED EPR lineshape seen in Fig. 1.

The $^3C_{70}$ ESE signal decays with τ increase were measured at a magnetic field position shown by arrow in Fig. 1. The representative results are given in Fig. 2 in a semilogarithmic scale. One can see that decays are nearly exponential. At temperatures below 85 K decays become "stretched" at large τ delays, which could be attributed to a distribution of relaxation times.

The transversal relaxation rates T_2^{-1} obtained at different temperatures from the initial slopes of the decay curves (like those shown in Fig. 2) are given in Fig. 3. One can see a sharp increase in the T_2^{-1} temperature dependence above 110 K for o-terphenyl [Fig. 3(a)] and above 100 K for decalin [Fig. 3(b)]. For comparison, in Fig. 3 also data on the T_2^{-1} temperature dependence for fullerene $^3C_{60}$ are given.[22] One can see that no sharp increase in this dependence takes place in the case of o-terphenyl [Fig. 3(a)], and in the case of decalin [Fig. 3(b)] the increase is much smoother than that seen for $^3C_{70}$.

The decays of the $^3C_{70}$ ESE signal with DAF increase also were measured at the field position indicated by arrow in Fig. 1, at a 120 ns τ delay between two microwave pulses. These decays were found (data not given) to be described by a stretched exponential function, $\exp(-(k_D T)^p)$, where k_D is the decay rate, T is the DAF, and p is an exponent, varying from 0.67 near 80 K until ~ 1 at higher temperatures. The best-fitted k_D values are also given in Fig. 3. These rates are much smaller than the T_2^{-1} values and manifest smooth and monotonic increase with temperature in the whole temperature range studied. From these data we conclude that decay of longitudinal magnetization and/or decay of the triplet state has no impact on the measured T_2^{-1} values.

IV. DISCUSSION

Figure 3 shows that T_2^{-1} for $^3C_{70}$ in molecular glasses of o-terphenyl and decalin manifests a sharp increase with tem-
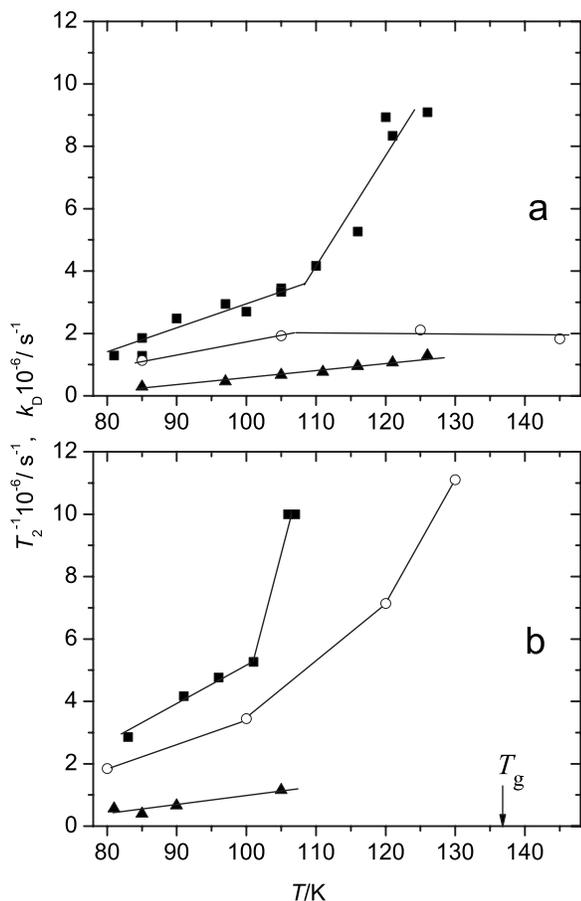
FIG. 3. Transversal relaxation rates T_2^{-1} obtained for $^3C_{70}$ photoinduced triplets (squares) in o-terphenyl (a) and decalin (b) glasses. For comparison, analogous T_2^{-1} data for $^3C_{60}$ also are given (open circles) (Ref. 22). There are shown also the k_D rates of the signal decay with DAF increasing (triangles). The lines are drawn to guide the eye. For decalin glass T_g value (137 K) is indicated.

perature, at some well-defined temperature points near 100 K. To discuss spin relaxation of $^3C_{70}$, we have to take into account the process of fast pseudorotation.[23–26] As pseudorotation is a quasivibrational motional process of the fullerene carbon atoms, it may be influenced by or even be coupled with vibrational motion of the surrounding atoms and molecules in the matrix. To suggest a model of such influence, we may take into account the experimental fact that $^3C_{60}$, although it experiences pseudorotation as well, nevertheless does not show an increase in the T_2^{-1} temperature dependence near 100 K, at least as sharp as the $^3C_{70}$ does (Fig. 3). The crucial difference between the $^3C_{70}$ and $^3C_{60}$ is that pseudorotation for the former is uniaxial while for the latter the direction of axial symmetry of the molecule may acquire different orientations in the matrix.[22] We suppose that sharp increase in spin relaxation for $^3C_{70}$ is related with fast iniaxial orientational motions of molecules (molecular librations) in the host matrix. Such librations may interact with pseudorotation of $^3C_{70}$, leaving pseudorotation of $^3C_{60}$ unaffected.

It is well known from numerous inelastic neutron and Raman scattering studies[2–6,28–31] that vibrational density of states in molecular glasses lie between 0 and ~150–200 cm^{-1}. In several works molecular librations

were postulated,[28–31] with the estimated librational frequencies lying typically in the range of several tens of cm^{-1}. Recent electron-nuclear double resonance (ENDOR) studies of librational motion of nitroxide spin probes in o-terphenyl glass[31] allowed directly obtaining librational frequency for a probe molecule as ~90 cm^{-1}. From these data one may estimate that near 100 K librations in glassy matrix indeed may be thermally excited. As the geometrical size of the fullerene molecule is much larger than that of a solvent molecule, the influence of molecular librations on the $^3C_{70}$ pseudorotation may be effective if librations have a cooperative nature, i.e., if they involve several cooperatively reorienting nearby molecules.

Neutron scattering studies of o-terphenyl[4,5] show that deviation of the atomic mean square displacement $\langle r^2 \rangle$ from a linear temperature dependence occurs at several temperatures. The most pronounced one takes place near 240 K (it is ascribed to T_d, see above). In Ref. 5 it was mentioned that such a deviation takes place also near 140 K. (In our opinion, data of Fig. 4 in Ref. 5, because of experimental uncertainty, may be interpreted as that the deviation starts near 120 K). Data in Ref. 4 (see Fig. 7 in this paper) clearly indicate the deviation near 100 K. Neutron scattering for decalin[6] show that deviation occurs near 80–100 K. As such deviations are related with changing of the type of vibrational motion, these results are in general agreement with the suggestion proposed here that near 100 K an additional vibrational process in the studied glassy matrices appears.

Usually additional transition seen near 100 K for proteins by neutron scattering is explained by methyl group rotation, because of the abundance of methyl groups in these media, and because their rotation enters at these temperatures into the time window of the experiment. However, in our case of decalin and o-terphenyl the matrices lack methyl groups at all, so this explanation is not applicable. The observed increase in the $^3C_{60}$ spin relaxation rate in decalin seen above 120 K [Fig. 3(b)] may be readily explained by the closeness of T_g in that case.

We may also note that nuclear magnetic resonance (NMR) data on probe molecules of nearly axial symmetry (benzene, hexamethylbenzene) in molecular glasses indicate the onset of uniaxial rotation occurring in a submillisecond time scale just near 100 K.[32–34] Probably this rotation of axially symmetric molecules and the pseudorotation of $^3C_{70}$ is influenced by the same dynamical processes in a glass. Note however that fullerene molecule has a larger size than these molecules studied by NMR and that the pseudorotation is much faster process than the ordinary rotation of a molecule.

V. CONCLUSIONS

The obtained results show that transverse spin relaxation rate T_2^{-1} for the $^3C_{70}$ fullerene photoexcited triplet state in molecular glasses manifests a sharp increase with temperature above 110 K in o-terphenyl glass and above 100 K in decalin glass (glass transition temperatures are essentially different for these two glasses, 243 and 137 K, respectively). This increase may be explained by interaction of $^3C_{70}$ pseu-

dorotation with molecular librations in the host matrix. Both motional processes involve vibrational motions of the atoms, and they may have therefore close amplitudes and time scale. Then, molecular librations in the matrix have a uniaxial character, which conforms to the $^3C_{70}$ pseudorotation mechanism.

In contrast, the $^3C_{60}$ triplet fullerene molecule, which experiences pseudorotation as well, does not show sharp increase in T_2^{-1} near 100 K, which is most probably because pseudorotation here is not uniaxial (i.e., the direction of the axial symmetry for $^3C_{60}$ may acquire different orientations in the matrix). So librations in the matrix may have no influence on the pseudorotation in that case.

The known literature data on Raman light scattering in molecular glasses[28–31] and ENDOR of embedded nitroxide spin probes[31] indicate that molecular librations may be thermally activated just near 100 K. It is also interesting to note that neutron scattering in o-terphenyl[4] and decalin[6] glasses near 100 K show a noticeable deviation of the structural mean square displacement $\langle r^2 \rangle$ from a linear temperature dependence, which also indicates on the onset here of additional vibrational motions.

As the fullerene molecule has a size much larger than that for the glass solvent molecules, it is likely that molecular librations in the matrix are of collective nature, i.e., they may involve several nearby molecules which reorient cooperatively. One may suppose that measurement of the $^3C_{70}$ spin relaxation in glassy materials (including polymers, etc.) may provide a sensitive tool to detect fast cooperative librations in these media.

ACKNOWLEDGMENTS

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