Photophysical properties of the extract of endometallofullerenes La@C_{2n} in *ortho*-dichlorobenzene. Picosecond laser photolysis

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The kinetics of relaxation of optical anisotropy induced by polarized light in endometallofullerenes La@C_{2n} in *ortho*-dichlorobenzene was studied by picosecond laser photolysis. Decay of the optical absorption signal due to the excited states of La@C_{2n} follows the biexponential law with two values of relaxation time: t_1 = 35±3 ps and t_2 = 1100±200 ps. The lifetime t or decay of the optical anisotropy is 19±5 ps and determined by the orientational diffusion of La@C_{2n}. The experimentally determined lifetime of optical anisotropy agrees satisfactorily with the value yielded by the theoretical model of orientational diffusion under slip boundary conditions at the interface of the La@C_{2n} molecule with the solvent.

Key words: endometallofullerenes, picosecond polarization spectroscopy, orientational relaxation.

We have recently proposed a new efficient procedure for isolation of endometallofullerenes from carbon black.[1] The procedure allows one to obtain extracts of endometallofullerenes La@C_{2n} in amounts sufficient for studying the photophysical and photochemical properties of these molecules. These extracts virtually do not contain "empty" fullerenes and represent a mixture of La@C_{82}, La@C_{80}, and La@C_{76}. The main component is La@C_{82} (70%). The configuration and structure of different isomers of La@C_{82} were studied by NMR and ESR spectroscopy.[2]

Experimental data on the kinetics of relaxation of electron-excited states of endometallofullerenes are presently lacking. In this work, we studied kinetic features of excited states that are necessary for understanding the interactions of electron states of the fullerene framework of C_{2n} and the La ligand and the interaction of the La@C_{82} molecule with the solvent. The character of the interaction with the solvent determines the solubility and degree of extraction of La@C_{82} from carbon black. The photophysical and photochemical properties of C_{60}, C_{70}, and some highest "empty" fullerenes have previously been studied in detail.[3,4] Relaxation of the excited π—π^*-states of C_{60} and C_{70} is mainly determined by the intersystem crossing S_1—T_1—S_0. The decay of S_1 and accumulation of T_1 states are described by the exponential law with a characteristic time of 1100 ps for C_{60} and 550 ps for C_{70}. The fast (7—10 ps) depolarization of the optical anisotropy (DOA) in experiments with picosecond polarization spectroscopy is a remarkable feature of fullerenes C_{60} and C_{70} in solutions. As has previously been shown, DOA of fullerenes can be due to two alternative mechanisms: rotational diffusion under slip conditions at the boundary of the molecule with the solvent and degeneration of electron states for high-symmetry C_{60} and C_{70} molecules. The second mechanism of depolarization is not valid for La@C_{2n} because of the low molecular symmetry of these molecules (C_{2v}). The boundary conditions on the fullerene—solvent interface are the same for C_{60}, C_{70}, and La@C_{2n} molecules. Comparative analysis of DOA for La@C_{2n}, C_{60}, and C_{70} molecules provides additional information about the nature of DOA of fullerene molecules in solutions. Since the extract of La@C_{2n} contains La@C_{82}, La@C_{80}, and La@C_{76} molecules with similar shape and volume, the mixture is a convenient object for studying the orientational mobility of the main component, La@C_{82}. In this work, the polarization laser photolysis technique was used to estimate the lifetime of the excited states of endometallofullerenes and the time of orientational relaxation of La@C_{82} in *ortho*-dichlorobenzene.

Experimental

Experiments were carried out by the polarization picosecond laser photolysis technique. A picosecond Nd^{3+} : glass laser with passive mode synchronization was used ($\lambda_{generation}$ = 1055 nm, pulse duration 6 ps). Excitation and probing were carried out by the second harmonic (λ_{exc} = 528 nm, λ_{prob} = 528 nm). The energy of the excitation pulse was equal to 1—5 μJ, and the energy of the probing pulse was ~10 times lower. The excitation pulse had a vertical polarization, and the probing pulse was polarized at an angle of 45° to the orientation of polarization of the excitation pulse. After passing

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through the sample, the probing pulse was decomposed by the Glan prism to two components with parallel $I_{\parallel}$ and perpendicular $I_{\perp}$ polarization axes relative to the direction of polarization of the excitation pulse. Intensities of two $I_{\parallel}$ and $I_{\perp}$ polarization axes were simultaneously detected by photodiodes, and the signals were amplified, transformed in the digital scale, and processed on a computer. Kinetic curves were recorded by the excitation—probing scheme.

Endometallofullerenes La@C_{2n} were synthesized and extracted according to the previously described procedure.[1] Mass spectral analysis showed that "empty" fullerenes were absent in the mixture. According to MS, La@C_{82} is the main component of the mixture (79%).

Experiments were carried out in a 5.0-mm cell at 23±1 °C. The optical density of the solution was D_{528} = 1.2 at a wavelength of 528 nm.

Results and Discussion

Lifetime of excited states for La@C_{2n} in ortho-dichlorobenzene. The kinetics describing the decay of the optical density induced by the picosecond excitation pulse for a solution of La@C_{2n} in *ortho*-dichlorobenzene is shown in Fig. 1, *a*. The biexponential law is valid for

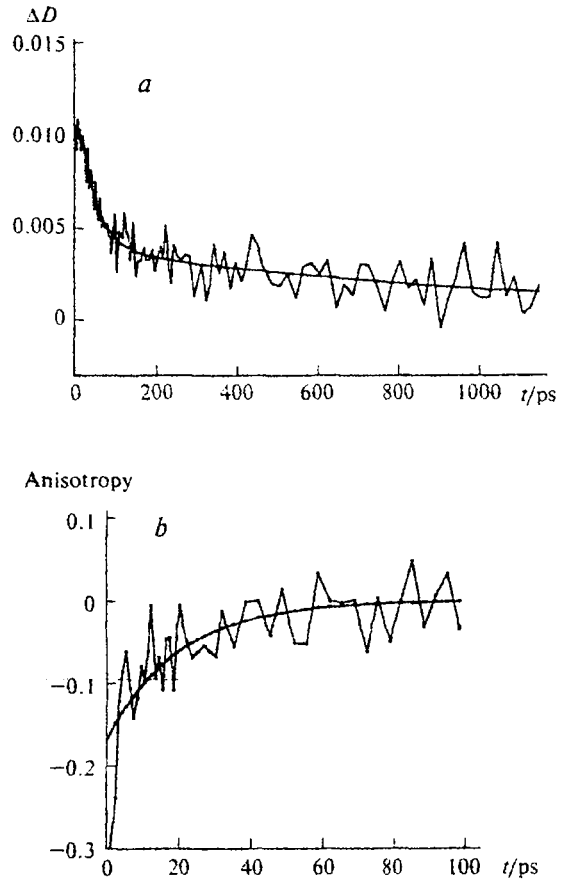

Fig. 1. Dependence of the differential optical density (*a*) and optical anisotropy (*b*) on the delay time for a solution of La@C_{2n} in *o*-dichlorobenzene; λ_{exc} = 528 nm, λ_{prob} = 528 nm.

the dependence of the optical density on the delay time t_1 = 35±3 ps and t_2 = 1100±200 ps. The signal from the excited states of La@C_{2n} was not observed in the spectral range from 400 to 1000 nm in experiments with nanosecond laser photolysis with the excitation at 532 nm and a time resolution of 50 ns. In the case of "empty" fullerenes C_{60} and C_{70}, the decay of the S_1 state with a characteristic time of 1100 ps for C_{60} and 550 ps for C_{70}[4] is observed, and an intense signal of T—T-absorption with a lifetime of ~40 μs is detected. Thus, La@C_{2n} is characterized by the complete relaxation of excited states when time is shorter than 50 ns. The short time of relaxation of the excitation in La@C_{2n} can be due to the formation of states with charge transfer between La and C_{2n} and to the effect of a heavy atom (La) for the intersystem local crossing in C_{2n}. The fast relaxation of the excitation through the state with charge transfer and due to the heavy atom effect as applied to fullerenes was discussed for the $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ and $(\eta_2\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_{60})$ complexes with τ = 43 ps[4] and τ = 18 ps,[5] respectively.

Optical anisotropy for La@C_{2n} in ortho-dichlorobenzene. The dependence of the optical anisotropy on the delay time for a solution of La@C_{2n} in *ortho*-dichlorobenzene is presented in Fig. 1, *b*. The optical anisotropy was determined by the expression

$$R(t) = (\Delta D_{\parallel} - \Delta D_{\perp})/(\Delta D_{\parallel} + 2\Delta D_{\perp}),$$

where $\Delta D_{\parallel}$ and $\Delta D_{\perp}$ are the differential optical densities for parallel and perpendicular polarization of probing relative to the polarization of excitation, respectively. The optical anisotropy in the zero moment of delay time $R_{t=0}$ determines the relative direction of the vectors of transition moments for the excitation $\mu_{S_0-S_1}$ and probing $\mu_{S_1-S_2}$ [6]:

$$R_{t=0} = 2/5[P_2(\mu_{S_0-S_1} \cdot \mu_{S_1-S_2})], \qquad (1)$$

where P_2 is the Legendre polynomial.

Using the experimental value $R_{t=0}$ = −0.2 and Eq. (1), we obtain the perpendicular direction of the vector of transition moment $\mu_{S_1-S_2}$ relative to the vector of transition moment $\mu_{S_0-S_1}$. The time of DOA is τ = 19±5 ps. Since La@C_{2n} is not characterized by degenerate electron states with symmetry T or higher, the fast DOA cannot be related to the loss of the coherent character between degenerate electron states.[7] Therefore, the kinetics of DOA for La@C_{2n} reflects the rotational dynamics of the molecules under study.

The rotational dynamics of La@C_{2n} can be analyzed theoretically. For different components of a mixture of La@C_{2n} ($2n$ = 82, 80, 76), the form and molecular weight change insignificantly; therefore, for dynamic calculations, the difference between the components may be ignored. The mixture consists predominantly of La@C_{82} molecules; therefore, the parameters of this molecule were used in further calculations. The most general expression for the time of orientational relax-

ation in terms of the Debye model is given in the form[8]:

$$\tau = (V\eta/kT) \cdot C \cdot f + t_0, \qquad (2)$$

where C is the coefficient in the equation describing the dependence of the relaxation time on the boundary conditions, which attains the values of 0 and 1 when the boundary conditions for slipping and sticking, respectively, are fulfilled; f is the coefficient that depends on geometric parameters of the molecule under study; V is the molecular volume of the molecule under study; η is the solvent viscosity; $\tau_0 = (2\pi/9) \cdot (I/k_BT)^{1/2}$ is the time of free rotation of the molecule under study; and I is its inertial moment. Under the boundary conditions for sticking (hydrodynamic conditions), $C = f = 1$, $t_0 = 0$. Accordingly, Eq. (2) becomes the Debye—Stokes—Einstein (DSE) equation. As is known, the DSE equation well describes rotation of many organic molecules in the liquid. Taking into account the van der Waals radius, the mean radius of the $La@C_{82}$ molecule was used as the radius of a ball with the equivalent volume $R = 5.63$ Å. The dynamic viscosity of *ortho*-dichlorobenzene is $\eta = 1.3$ cP. The inertial moment of $La@C_{82}$ $I = 2.7 \cdot 10^{-36}$ g cm^2 was calculated from the noncentral arrangement of the La atom in the $La@C_{82}$ molecule.[9] The found inertial moment determines the time of free rotation of $La@C_{82}$ in the gas at room temperature $\tau_0 = 5.6$ ps. According to the DSE equation, the relaxation time calculated for the $La@C_{82}$ molecule in *ortho*-dichlorobenzene was 238 ps, which is much higher than the experimental time of the optical anisotropy decay. The Cf coefficient in the DSE equation, which reflects the degree of slipping of $La@C_{82}$ in the solution, is equal to 0.056. The microscopic theory of molecular dynamics[10] under assumption of boundary conditions for slipping, was used for the description of rotation of the molecule. In this theory, the linear and angular moments of the molecule under study are transmitted into the layer of nearest molecules through collisions, and this transfer is described by the rough sphere model of the liquid. According to this theory, the C coefficient in Eq. (2) is calculated from the microscopic parameters of the molecule and solvent molecules, such as the mass, inertial moment, and geometric size. Using the microscopic parameters of the molecule under study and the solvent molecule, the C coefficient can be calculated and the assumed relaxation time of the molecule under study can be found. The inertial moment $I = 1 \cdot 10^{-37}$ g cm^2, the mean radius $R = 2.86$ Å, and the density of *ortho*-dichlorobenzene $d = 1.3$ g cm^{-3} were used for the calculation.

The relaxation time τ thus determined was 24 ps, which agrees satisfactorily with the experimental value of 19±5 ps.

Thus, as shown previously for molecules of fullerenes C_{60} and C_{70},[3] the dynamics of rotation of the $La@C_{82}$ molecule can be described by the microscopic models of molecular dynamics when slipping conditions are valid at the boundary with the solvent. As in the case of fullerenes C_{60} and C_{70}, this is related to a high symmetry of the framework of the $La@C_{82}$ molecule, which decreases steric hindrances during rotation of these molecules in the solution.

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