Orientational dynamics of C_{70} molecules in chlorobenzene

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Dynamics of anisotropy relaxation of C_{70} singlet excited molecules in chlorobenzene was measured at room temperature by the picosecond transient grating technique. The time-dependent diffraction efficiency exhibits a two-stage decay: a fast component (τ_1 = 12±5 ps), which is comparable with the corresponding signal of C_{60} in chlorobenzene (τ = 8±2 ps), and a slow one (τ_2 = 30±5 ps). It is supposed that relaxation of anisotropy is related to the orientational mobility of excited C_{70} molecules relative to two axes of the molecular framework. The results obtained cannot be described by the Einstein—Stokes—Debye theory. The Hynes—Kapral—Weinberg theory, which takes into account microscopic interactions between molecules upon collisions, agrees satisfactorily with the experiment. The influence of dielectric friction on the orientational mobility of C_{70} in chlorobenzene was estimated.

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

Considerable attention has been given to fullerenes, which is related to the unique properties of these molecules, *e.g.*, the unusually high mobility of C_{60} and C_{70} molecules in the solid and liquid phases.[1—8] Orientational relaxation of C_{60} in solutions was studied by ^{13}C NMR,[1—5] ESR,[6] and fluorescence polarization[7] spectroscopies. The orientational relaxation time of C_{60} in tetrachloroethane[1] measured by ^{13}C NMR spectroscopy at 283 K was 15.5 ps, 16 ps in carbon disulfide[2] at 298 K, and 16.9 ps in deuterated toluene[3] at 303 K. As far as we know, no studies on the orientational dynamics of C_{70} in solutions have been performed so far.

We have previously studied[8] the orientational dynamics of a C_{60} molecule in several organic solvents by the picosecond transient grating technique. The observed signals of anisotropy relaxation of singlet excited C_{60} molecules were assigned to the orientational dynamics of the molecular framework. The times of orientational relaxation obtained turned out to be considerably lower than those predicted by the Einstein—Stokes—Debye (ESD) equation. Good agreement with experiment was obtained within the framework of the microscopic Hynes—Kapral—Weinberg (HKW) theory.[9] Unusually short times of orientational relaxation of a C_{60} molecule were observed in decalin and toluene solutions, in which the orientational motion is likely inertial and is not determined by diffusion.

In this work, the orientational mobility of C_{70} in chlorobenzene was studied by the picosecond transient phase grating technique.

Experimental

Details of the picosecond setup were described previously.[8] Unlike C_{60}, the extinction coefficient of the triplet excited state of a C_{70} molecule ($\varepsilon_{T_1-T_2}$) is approximately twice that of the singlet excited state $\varepsilon_{S_1-S_2} \leq 2 \cdot 10^3$ mol^{-1} L cm^{-1} (see Refs. 10—12). Therefore, the picosecond transient phase grating technique with crossed polarization of exciting beams was used to prevent the effect of long-lived triplet and heat gratings. A neodymium-glass laser with passive mode synchronization was used as a source of picosecond pulses. The generation wavelength was 1055 nm, and the pulse duration after an optical modulator and an amplifying system was 6.2 ps. Light of the second harmonic light with wavelength 528 nm was used for excitation of the C_{70} molecule.

To create the transient phase grating, two light excitation pulses simultaneously converged on the sample. When the polarizations of excitation pulses are perpendicular, their interference results only in the distribution of directions of the polarization vector,[13] due to which only the phase grating of moment directions of the singlet excited C_{70} molecule transition is induced in the sample. Excited C_{70} molecules were probed by light of the first harmonic at 1055 nm. The probe pulse was polarized at an angle of 45° to the polarization of excitation pulses and diffracted on the phase grating formed.

Each point in the kinetic dependence was recorded during one laser pulse in an automatic mode, and the time delay of the probe pulse was established relative to excitation pulses. The diffraction signal was recorded and recovered, taking into account intensities of excitation and probe pulses..

The excitation pulse energy was 1 to 5 μJ. The probe pulse energy was approximately tenfold lower. Sizes of the grating and probe areas were 250 to 300 μm and 200 μm, respectively. The diffraction signal was registered by a photodiode, ampli-

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fied, digitized, and processed on a computer. Experiments were carried out in a cell 1.0 mm in width at 23±1 °C. Concentrations of C_{60} and C_{70} were $3 \cdot 10^{-3}$ and $1.7 \cdot 10^{-3}$ mol L^{-1}, respectively.

Results and Discussion

The dependences of the diffraction efficiency on the time delay for chlorobenzene solutions of C_{60} and C_{70} are presented in Fig. 1. It should be mentioned that the signal recorded contains a nonresonance component of the pure solvent along with a resonance component of the dissolved fullerene molecules. The experiment with the pure solvent shows that the relative contribution of the solvent to the total signal does not exceed 20 %. In addition, the characteristic time of the signal of chlorobenzene caused by orientational relaxation of molecules is sufficiently low: ~6 ps according to the literature data[14] and our estimations.[15] The low contribution to the total signal and relatively short characteristic time make it possible to neglect the solvent effect at times greater than 10 ps. In this region, the time dependence of the signal is not monoexponential, and two characteristic times of relaxation are distinctly seen, which is related, in our opinion, to the anisotropy of orientational motion of a C_{70} molecule. The form of the C_{70} molecule is presented with high accuracy by a rotational ellipsoid. The equation for the anisotropy of rotational diffusion of the rotational ellipsoid was obtained by Perrin[16]

$$r(t) = (2/5)\,[a_1\exp(-k_1 t) + a_2\exp(-k_2 t) + a_3\exp(-k_3 t)], \quad (1)$$

where a_1, a_2, and a_3 are constants depending on the angle between the transition moment and rotational axis of the ellipsoid; $k_1 = 6D_\perp$, $k_2 = 5D_\perp + D_\parallel$, and $k_3 = 2D_\perp + 4D_\parallel$; and $D_\parallel$ and $D_\perp$ are the coefficients of rotational diffusion around and across the rotational axis of the ellipsoid, respectively. When the transition moment is perpendicular to the rotational axis of the ellipsoid, $a_1 = 1/4$, $a_2 = 0$, $a_3 = 3/4$, and the time dependence of the anisotropy is expressed as the sum of two exponentials.

The diffraction efficiency for the configuration of pulse excitation with crossed polarization can be presented in the form[17]

$$\begin{aligned}\eta(t) &\approx \exp(-2t/\tau_s) \cdot r(t)^2 \approx \\ &\approx \exp(-2t/\tau_s) \cdot [A\exp(-t/\tau_1) + B\exp(-t/\tau_2)]^2, \quad (2)\end{aligned}$$

where

$$\tau_1 = (2D_\perp + 4D_\parallel)^{-1}, \quad (3)$$

$$\tau_2 = (6D_\perp t)^{-1}, \quad (4)$$

A and B are constants and τ_s is the lifetime of the excited state.

For the C_{70} molecule, τ_s ~550 ps.[10,11] Processing of the experimental data using Eq. (2) allowed one to obtain the following values: τ_1 = 12±5 ps and τ_2 = 30±5 ps. Writing the times of orientational relaxation around and across the rotational axis of the ellipsoid of the C_{70} molecule in the form

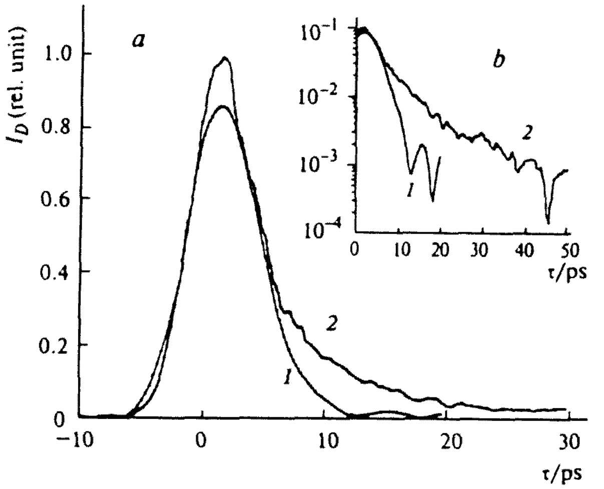

Fig. 1. *a.* Dependences of the diffraction efficiency (I_D) on the time delay (τ) for C_{60} (*1*) and C_{70} (*2*) in chlorobenzene. *b.* Logarithm of the diffraction efficiency.

$$\tau_{\parallel,\perp} = 1/6D_{\parallel,\perp}, \quad (5)$$

and using Eqs. (3), (4), and (5), we obtain

$$\begin{aligned}\tau_\perp &= \tau_2, \\ \tau_\parallel &= (2/3)[1/\tau_1 - 1/(3\tau_2)]^{-1}. \quad (6)\end{aligned}$$

Substituting the τ_1 and τ_2 values into Eq. (6), we determine the time of orientational relaxation around the rotational axis of the ellipsoid of the C_{70} molecule: $\tau_\parallel$ = 9±5 ps. The experimentally obtained ratio of the A and B coefficients in Eq. (2) (A/B = 3±0.5) confirms the perpendicular orientation of the transition moment to the rotational axis of the ellipsoid of C_{70}.

The hydrodynamic ESD theory and HKW theory were used for analysis of the data obtained. Diffusion coefficients were calculated by the Einstein equation:

$$D_{\parallel,\perp} = k_B T/\xi_{\parallel,\perp}, \quad (7)$$

where $\xi_{\parallel,\perp}$ is the coefficients of rotational friction relative to the long and short axes of the ellipsoid of the C_{70} molecule.

In the hydrodynamic ESD approximation

$$\tau_{\parallel,\perp}{}^{hd} = \xi_{\parallel,\perp}{}^{hd}/6k_bT + \tau_0, \quad (8)$$

$$\xi_{\parallel,\perp}{}^{hd} = 8\pi\eta R^3 f_{\parallel,\perp}, \quad (9)$$

where R is the mean diameter of the molecule under study; η is the dynamic viscosity of the solvent; $f_{\parallel,\perp}$ is a coefficient equal to the Perrin factors in the case of boundary conditions[16] and can be determined by the tabulated dependence,[18] $\tau_0 = (2\pi/9) \cdot (I/k_BT)^{1/2}$ (τ_0 is the time of free rotation of the molecule studied and I is its inertia moment) under slip conditions. Taking into account van der Waals radii, the framework of the C_{70} molecule is described by an ellipsoid with lengths of semiaxes 5.85 and 5.15 Å. The mean radius of the C_{70} molecule was taken to be equal to the radius of a ball of equivalent volume (R = 5.37 Å). The dynamic viscosity of chlorobenzene (η) is equal to 0.8 cP. The times of orientational relaxation ($\tau_{\parallel}{}^{hd}$ = 120 ps and $\tau_{\perp}{}^{hd}$ = 131 ps) calculated from Eqs. (8) and (9) under stick conditions ($f_{\parallel}{}^{st}$ = 0.952 and $f_{\perp}{}^{st}$ = 1.036) are considerably higher than the corresponding experimental values. The calculation under slip conditions ($f_{\parallel}{}^{sl}$ = 0 and $f_{\perp}{}^{sl}$ = 0.01) give understated results: $\tau_{\parallel}{}^{sl}$ = 4 ps and $\tau_{\perp}{}^{sl}$ = 5 ps.

It is likely that the difficulties of description of orientational relaxation of C_{60} and C_{70} molecules within the framework of the hydrodynamic model are associated with the fact that stick and slip conditions are not fulfilled at the boundaries of these molecules upon their motion in solvent. The arrangement of the nearest-neighbor molecules is almost uninfringed upon orientational motion of the spherelike C_{60} and C_{70} molecules, which weakens friction and can result in the slip effect. A similar result was observed for the translational movement of C_{60} in benzene.[19] At the same time, no complete slip is observed, which testifies to the interaction between the molecule studied and solvent molecules. It seems impossible to estimate this interaction in terms of the ESD equation.

In several works, the microscopic HKW theory[9] was successfully used for description of rotational and translational movements of spherelike molecules. This theory considers the influence of microscopic (collisions) and collective (hydrodynamic) effects. In this model, linear and angular moments of the molecule studied are transmitted to the layer of adjacent surrounding molecules upon collisions. This transfer is described on the basis of the rough sphere fluid theory. According to this model, the coefficient of rotational friction equals

$$\xi_{\parallel,\perp}{}^{\mathrm{HKW}} = \xi_E \xi_{\parallel,\perp}{}^{hd}/(\xi_E + \xi_{\parallel,\perp}{}^{hd}), \qquad (10)$$

$$\xi_E = (8/3)\cdot\pi\beta R^3, \qquad (11)$$

where $\xi_{\parallel,\perp}{}^{hd}$ is taken under slip conditions and β is the slip coefficient, which characterizes the extent of microscopic interaction between the molecule studied and solvent molecules upon collisions. When $\beta \to 0$, the slip boundary conditions are fulfilled and $\xi_{\parallel,\perp}{}^{\mathrm{HKW}} \to 0$; in the case $\beta \to \infty$, the slip conditions corresponding to the hydrodynamic regime and according to Eqs. (10) and (11) are the following: $\xi_{\parallel,\perp}{}^{\mathrm{HKW}} \to \xi_{\parallel,\perp}{}^{hd}$.

The slip coefficient can be calculated from the microscopic parameters of the molecule under study and the solvent molecule

$$\beta = [K_b/(1 + K_{ab})](2\gamma k_B T/\pi)^{1/2} \rho g_{ab} R(1 + r/R)^2, \qquad (12)$$

where g = $m_a m_b/(m_a + m_b)$ is the adduced mass; m_a and m_b are masses of the solvent molecule and the molecule under study, respectively; r and R are the radii of the solvent molecule and the molecule under study, respectively; ρ is the number of solvent molecules per unit volume; g_{ab} is the function of the radial distribution of molecules[20]; $K_a = I_a/m_a r^2$, $K_b = I_b/m_b R^2$, and $K_{ab}{}^{-1} = \gamma[(m_a K_a)^{-1} + (m_b K_b)^{-1}]$ are the adjusted inertia moments; and I_a and I_b are the inertia moments of the solvent molecule and the molecule studied, respectively.

It follows from Eqs. (10), (11), and (12) that the hydrodynamic regime for spherical molecules takes place under the condition where $\xi_{\parallel,\perp}{}^{hd}/\xi_E = 3\eta/\beta \ll 1$. For fullerene C_{70} dissolved in chlorobenzene, $3\eta/\beta \cong 7$, and, according to this model, the hydrodynamic regime is not fulfilled. Using Eqs. (5), (7), (10), (11), and (12), we obtained the times of orientational relaxation $\tau_{\parallel}{}^{\mathrm{HKW}}$ = 12 ps and $\tau_{\perp}{}^{\mathrm{HKW}}$ = 15 ps. The times obtained are closer to the real ones, but the relaxation time $\tau_{\perp}{}^{\mathrm{HKW}}$ is considerably lower than the experimental one.

The dielectric friction considerably affects the rotational mobility of polar molecules. Unlike C_{60}, the charge distribution in the C_{70} molecule is nonuniform.[21,22] This should result in the polarization of surrounding molecules and appearance of the dielectric friction. Since the charge distribution in the C_{70} molecule is symmetric, the dipole moment for the whole molecule is equal to zero. The absence of the constant dipolar moment does not allow one to use the Nee—Zwanzig correlation[23] for estimation of the dielectric friction coefficient. To solve this problem, we used an approach suggested by Alavi and Waldeck.[24] These authors obtained the equation for the dielectric friction coefficient that makes it possible to take into account the charge distribution in the molecule

$$\xi_{DE} = \frac{8}{a}\frac{(\varepsilon_S - 1)}{(2\varepsilon_S + 1)^2}\tau_D \cdot \sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{L=1}^{\infty}\sum_{M=1}^{L} A \cdot M^3 \cdot B, \qquad (13)$$

where $A = \left(\frac{2L+1}{L+1}\right)\frac{(L-M)!}{(L+M)!}$,

$$\mathrm{B} = q_i q_j \left(\frac{r_i}{a}\right)^L \left(\frac{r_j}{a}\right)^L P_L^M(\cos\theta_i) P_L^M(\cos\theta_j)\cos(M\varphi_{ji}),$$

where $P_L{}^M(x)$ are Legendre polynomials, a is the radius of the area in which the molecule under study is present, N is the number of the charge, and q_i is the charge on the ith atom. The position of the ith atom is specified in the spherical system of coordinates (r_i, θ_i, φ_i), $\varphi_{ji} = \varphi_j - \varphi_i$, τ_D is the time of dielectric relaxation of solvent molecules, and ε_s is the static dielectric constant of the solvent. Two variants of charge distribution on atoms in the C_{70} molecule taken from Refs. 21 and 22 were used for calculation by Eq. (13). The value of a was taken equal to the mean radius of the C_{70} molecule, taking into account van der Waals radii; static dielectric constant of chlorobenzene ε_s = 5.7; and dielectric relaxation time of chlorobenzene τ_D = 12.5 ps.[25] Since the axis of symmetry of the charge distribution in the C_{70} molecule coincides with the axis of rotation of this molecule, the dielectric friction coefficient ξ_{DE} enters only into the equation for $D_{\perp}$: $D_{\perp} = k_BT/(\xi_{\perp} + \xi_{DE})$, and

$$\tau_{DE} = \xi_{DE}/6k_BT \qquad (14)$$

should be added to the time of orientational relaxation around the short axis of the ellipsoid.

Using Eqs. (13) and (14), we obtained the values of τ_{DE} equal to 5 and 7 ps for two different variants of charge distribution taken from Refs. 21 and 22, respectively.

Taking into account the dielectric friction, the total time of orientational relaxation around the short axis of the ellipsoid in the HKW model is 20 to 22 ps and close to the experimental value.

Thus, the dynamics of anisotropy relaxation of excited C_{70} molecules in chlorobenzene was measured by the picosecond transient grating technique. The possibility of explaining time parameters of the experimental signal using concepts of the orientational motion of the molecular framework was shown. The hydrodynamic ESD approach cannot explain the short times of orientational relaxation observed in experiments. The HKW model, which takes into account microscopic aspects of collision interactions between the molecule under study and solvent molecules, is the most appropriate for description of the orientational motion of such spherelike molecules as C_{60} and C_{70}. The dielectric friction coefficient of the C_{70} molecule in chlorobenzene was determined and the addition to the orientational relaxation time was estimated from the charge distribution on atoms in the C_{70} molecule.

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