Orientational rotation of C_{60} molecules in various solutions

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Polarization relaxation of C_{60} molecules has been studied experimentally in various solvents. The results can be described well by a rough-sphere model, as a rotation of C_{60} molecules. © *1994 American Institute of Physics.*

Research on the orientational rotation of molecules in liquids has attracted considerable interest, since the rotation of molecules and fragments of molecules frequently determines the mechanism and efficiency of chemical reactions. The rotation of most dye molecules can be described by the Debye–Stokes–Einstein hydrodynamic theory,[1–3] which predicts a linear dependence of the orientational relaxation time on the viscosity of the solvent.

In this letter we are reporting a study of the rotation of C_{60} molecules in various solvents: toluene, orthoxylene, orthodichlorobenzene and decalin. We used a method of induced gratings. We analyze the experimental data on the basis of the Debye theory and also on the basis of a microscopic rough-sphere theory,[4,5] which applies to the rotation of small spherical molecules.

The induced-grating method is described in detail in the literature.[6,7] The induced-grating experiments were carried out on an apparatus developed by us.[8] We used a neodymium-glass laser ($\lambda=1055$ nm) with a pulse length $\tau_{1/2}=6.2$ ps. The polarization of each of the exciting beams ($\lambda=528$ nm) was parallel to the x axis (Fig. 1). The energy of each of the beam which was incident on the sample and which formed the grating was typically 1–5 μJ; the energy in the probe beam was lower by a factor ~ 10. The size of the excitation zone was $\sim$250–300 μm, and that of the probe zone $\sim$200 μm. The polarization of the probe beam ($\lambda=1055$ nm) made an angle of 45° with the x axis (Fig. 1). The diffracted beam was broken up into two components by a Glan prism: one with polarization parallel to the exciting beams ($\|$) and one with polarization perpendicular to these beams ($\perp$). All experiments were carried out at $23\pm1\,^\circ$C. The C_{60} concentration was $(0.5–1)\times10^{-3}$ M. The extinction coefficient of the singlet excited state of C_{60} at a probe wavelength of 1.06 μm is[9] $\sim(0.7–1.2)\times10^4(\mathrm{M\cdot cm})^{-1}$. The lifetime of the C_{60} excited state in toluene is[9] 950 ps. The actual signal was reconstructed by dividing by the intensity of the excitation signal raised to the third power.

The time evolution of the diffracting signal is analyzed in detail in Refs. 6 and 7. For δ-function probe and excitation pulses we have

$$I_{\|}(t)=K[1+2r(t)]^2\exp(-2t/\tau_{\mathrm{si}}), \tag{1}$$

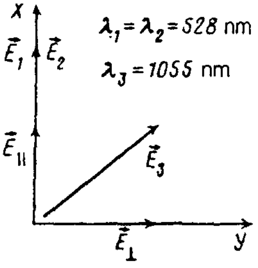

FIG. 1. Polarizations of the exciting beams ($\mathbf{E}_1$,$\mathbf{E}_2$), of the probe beam ($\mathbf{E}_3$), and of the measured diffracted beams ($\mathbf{E}_\parallel$ and $\mathbf{E}_\perp$) in an induced-grating experiment.

$$I_\perp(t) = K[1 - r(t)]^2 \exp(-2t/\tau_{si}), \tag{2}$$

where $I_\parallel(t)$ and $I_\perp(t)$ are the intensities of the diffracted light for the cases of respectively parallel and perpendicular polarization of the probe, K is a normalization factor, τ_{si} is the lifetime of the excited state of the molecule under study, and $r(t)$ is the anisotropy. For isotropic rotational diffusion we have

$$r(t) = r_0 \exp(-t/\tau_r), \quad r_0 = \frac{2}{5} P_2(\cos\varphi), \tag{3}$$

where τ_r is the orientational rotation time, φ is the angle between the moments of the S_0–S_1 and S_1–S_2 transitions, and P_2 is the Legendre polynomial of index 2 (Ref. 2). If the transition moments are parallel (i.e., if $\varphi = 0$), then the anisotropy at $t = 0$ is $r_0 = 0.4$. In an actual experiment, even with $\varphi = 0$, the value of r_0 is usually smaller than 0.4, because of the imperfect quality of the grating and possible saturation of the grating.

Figure 2 shows experimental curves of the time evolution of the diffraction efficiency for the cases of parallel and perpendicular probe polarizations, as found for C_{60} solutions in four different solvents. The typical rotation times of the C_{60} molecule are seen to be quite different in these solvents. The shortest time is observed in decalin, which is the most viscous of the solvents, while the longest is observed in orthoxylene. Since τ_r for decalin is smaller than the length of the laser pulse, the difference between the parallel and perpendicular signals is "smeared" because of this circumstance. A corresponding effect was observed in toluene.

Figure 3 shows the time evolution of the anisotropy as calculated from

$$r(t) = (\sqrt{I_\parallel} - \sqrt{I_\perp})/(\sqrt{I_\parallel} + 2\sqrt{I_\perp}) = r_0 \exp(-t/\tau_r). \tag{4}$$

For times greater than 5–6 ps the effect of a nonzero pulse length becomes negligible. We approximated the points in part of the figure by a straight line for the time dependence of $\ln r$. From this line we determined the value of τ_r. The solid lines in Figs. 2 and 3 are the results of calculations carried out as a convolution of expressions (1) and (2) and the functions which determine the shape of the excitation and probe pulses.

Two models were used to describe the resulting data. The first is based on the hydrodynamic approximation of the Debye theory, in which the solvent is treated as a continuous medium characterized by a viscosity η. In the case of "stick" boundary conditions,[1] the rotation diffusion coefficient D_s is

$$D_s = kT/8\pi\eta R^3, \tag{5}$$

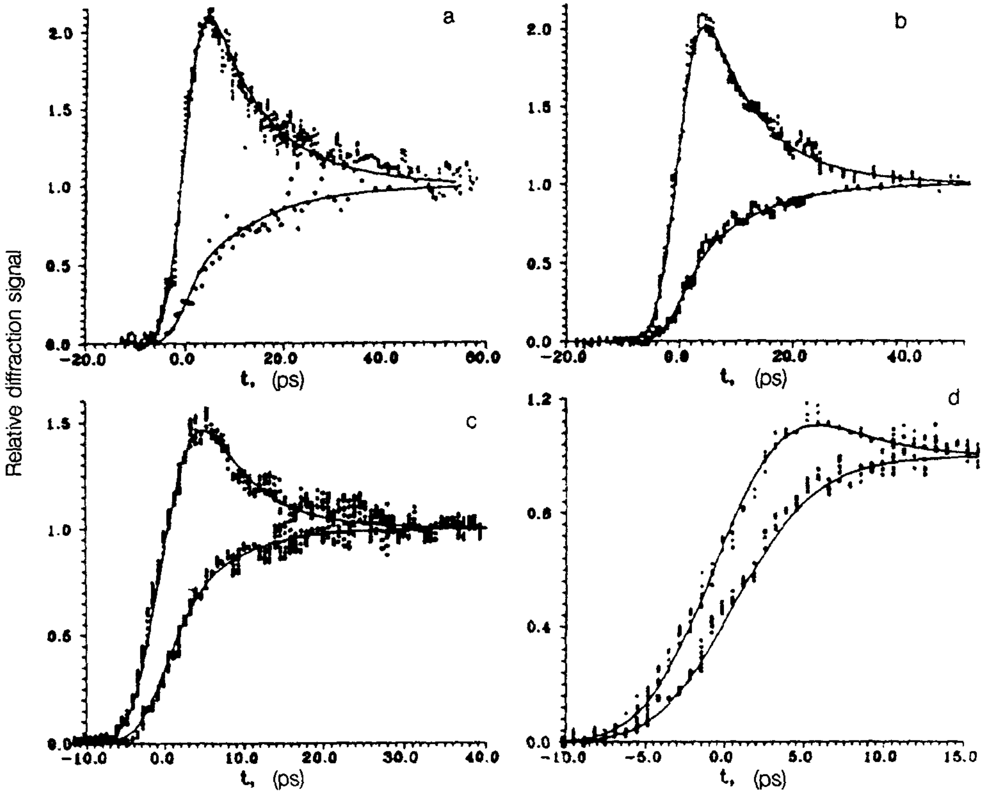

FIG. 2. Time evolution of the diffraction signal of C_{60} in various solvents for parallel and perpendicular polarizations of the signal. a—In orthoxylene; b—in orthodichlorobenzene; c—in toluene; d—in decalin. $\lambda_{\text{exc}}=528$ nm, $\lambda_{\text{probe}}=1055$ nm. The intensities of the parallel and perpendicular signals have been normalized. The solid curves here and in Fig. 3 are the results of calculations incorporating the length of the excitation and probe pulses.

where R is the radius of the rotating molecule, k is the Boltzmann constant, and T is the temperature. The time scale of the orientational relaxation was written in the form $\tau_s=(6D_s)^{-1}$. Table I shows the results of calculations of D_s and τ_s (the radius of the C_{60} molecule was taken to be 5.15 Å). The semiempirical approach which is taken in the Debye theory with the help of a slipping coefficient ("slip" boundary) cannot be taken in the case of C_{60}, since the orientational relaxation time is independent of the type of solvent for spherical molecules in this case. This time is equal to the time scale of free rotation without collisions.

The second model is based on the theory of rough spheres.[4,10] The collision dynamics in this theory is governed by the conservation laws for linear and angular momentum. It depends on the masses and sizes of the colliding particles and the density of the solution. According to the Enskog kinetic theory,[4,5,10] the rotational diffusion coefficient can be written

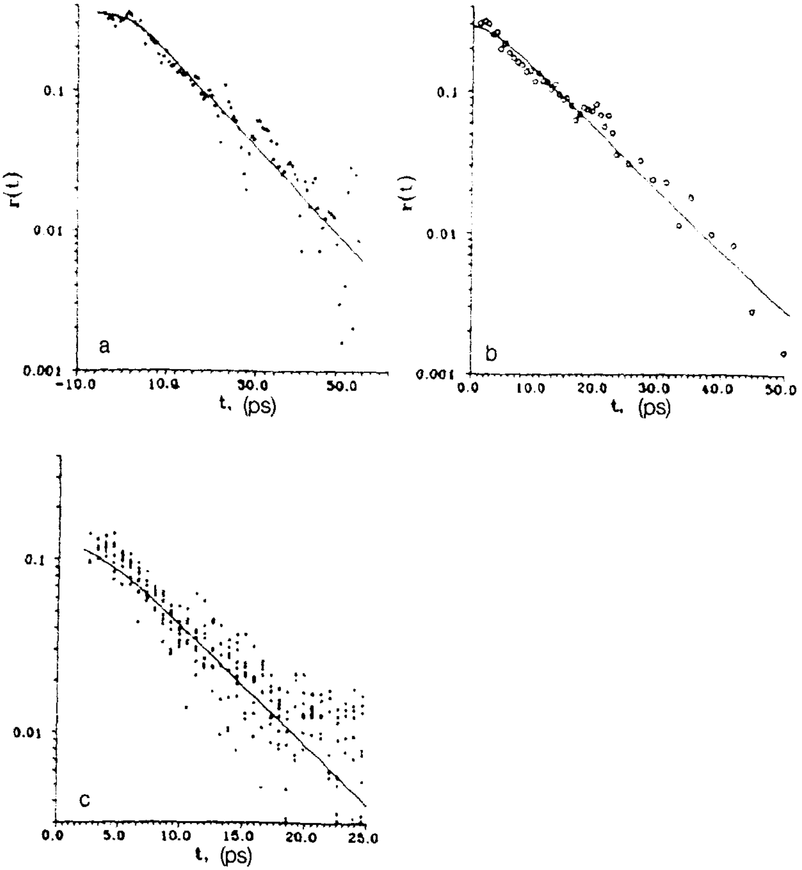

FIG. 3. Time evolution of the anisotropy, $r(t)$, for C_{60}. a—In orthoxylene; b—in orthodichlorobenzene; c—in toluene.

$$D_e^{-1}=\frac{8}{3}\left(\frac{B}{1+b'}\right)\left(\frac{2\pi\gamma}{kT}\right)^{1/2}\left(1+\frac{r}{R}\right)^2\rho R^4 g(R+r), \tag{6}$$

where R and r are the radii of the test molecule and the molecule of the medium, respectively; ρ is the density of the solvent (in cm^{-3}); $g(R+r)$ is the coefficient of the distribution of contact pairs; γ is the reduced mass; and we have $(b')^{-1}=\gamma[(MB)^{-1}+(mb)^{-1}]$, where M and m are the masses of the test molecule and the molecule of the medium, respectively, and B and b are their reduced moments of inertia. According to Ref. 11, the reduced orientational time τ^* is related to the rotational diffusion coefficient D^* (for $D^*<2$) by

$$\tau^*=\frac{1}{6D^*}M(1.1+6D^{*2}), \tag{7}$$

TABLE I. Experimental and theoretical time scales and diffusion coefficients of the orientational rotation of C_{60} in various solvents. The calculations were carried out from the Debye theory (D_s, τ_s) and the rough-sphere theory (D_e, τ_e).

	ρ $cm^{-3}\cdot 10^{21}$	r, Å	η, cP	D_s $c^{-1}\cdot 10^9$	D_e $c^{-1}\cdot 10^9$	τ_s ps	τ_e ps	τ_{expt} ps
Toluene	5.65	2.7	0.590	2.0	21	83.5	8.5	7.0 ± 1.5
Orthoxylene	4.98	2.8	0.810	1.5	23	113	7.9	13 ± 2
Orthodichlorobenzene	5.306	2.8	1.324	0.92	16	181	11.1	10.3 ± 1.5
Decalin	3.82	2.9	2.150	0.5	38	334	5.2	3.5 ± 1.5

where $M()$ is the Kummer function, $D^* = D(I/kT)^{1/2}$, $\tau^* = \tau(kT/I)^{1/2}$, and I is the moment of inertia of the molecule. The results of calculations of τ_e in terms of D_e from (7) are shown in Table I.

It can be seen from this table that the Debye theory predicts orientational rotation times which are far too long. Nor do we see the predicted linear dependence of τ on the viscosity: For the most viscous solvent, τ_{expt} is at its shortest. The rough-sphere model works better: The values calculated for decalin, orthodichlorobenzene, and toluene essentially agree with the experimental data. The measured value of τ for orthoxylene is longer than the theoretical value, apparently because of characteristic features of the intermolecular interaction of C_{60} with this solvent, which leads to an increase in the "friction" during the rotation of the C_{60} molecules.

Interestingly, the rough-sphere theory predicts a nearly free rotation of C_{60} in decalin (according to Ref. 12, the free-rotation time of C_{60} is 3.1 ps at 10°C). To a large extent, this result occurs because this solvent has the smallest density ρ. As a result, the C_{60} molecule has its lowest collision rate in decalin. This circumstance is probably responsible for the smaller value of τ.

According to Ref. 13, the rotation of molecules becomes inertial rather than diffusive under the condition $\tau/\tau_{fr} \leqslant 2$, where $\tau_{fr} = 2\pi/9 \times (I/kT)^{1/2}$ is the free-rotation time of the molecule, and I is the moment of inertia of the molecule. For decalin we have a ratio $\tau_{expt}/\tau_{fr} \sim 1$, while for toluene this ratio is ~ 2.2. The mechanism for the rotation of C_{60} in decalin and, possibly, in toluene is thus not diffusive. In this connection, we see why a description of the rotation in decalin as exponential, in accordance with (3), is valid only for estimates.

Here are some possible reasons why the Debye theory fails to describe the experimental data: a) Stick boundary conditions do not hold for the spherical C_{60} molecule. b) The Debye theory assumes a diffusive mechanism for the motion, while the rotation of C_{60} in decalin and toluene is apparently inertial in nature.

In summary, this study has yielded experimental results on the polarization-relaxation signal of C_{60} molecules as a function of the time in various solvents. The behavior can be described fairly well by the microscopic rough-sphere model as a rotation of C_{60} molecules. There is the further possibility that the observed signal may be influenced by an exchange between different deformation states of the core of the molecule (e.g., between Jahn-Teller states[14]).

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[1] P. Debye, *Polar Molecules* (Dover, New York, 1929).
[2] A. B. Myers and R. M. Hochstrasser, J. Quant. Electron. **QE-22**, 1482 (1986).
[3] A. Von Jena and H. E. Lessing, Chem. Phys. **40**, 245 (1979); Chem. Phys. Lett. **78**, 187 (1981).
[4] J. O'Dell and B. J. Berne, J. Chem. Phys. **63**, 2376 (1975).
[5] J. T. Hynes *et al.*, J. Chem. Phys. **69**, 2725 (1978).
[6] H. J. Eichler *et al.*, *Laser-Induced Dynamic Gratings* (Springer-Verlag, New York, 1986).
[7] A. Von Jena and H. E. Lessing, Opt. Quantum Electron. **11**, 419 (1979).
[8] I. V. Rubtsov *et al.*, Khim. Fiz., 1995 (in press).
[9] V. A. Nadtochenko *et al.*, Photochem. Photobiol. A **70**, 153 (1993).
[10] H. T. Davis and G. Subramanian, Phys. Rev. A **11**, 1430 (1975).
[11] M. Fixman and K. Rider, J. Chem. Phys. **51**, 2425 (1969).
[12] R. D. Johnson *et al.*, Science **255**, 1235 (1991).
[13] W. A. Steele, J. Chem. Phys. **38**, 2411 (1963).
[14] A. Regev *et al.*, J. Phys. Chem. **97**, 3671 (1993).

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