STUDIES OF EFFECTS OF HYDROGEN BONDING ON ORIENTATIONAL RELAXATION USING PICOSECOND LIGHT PULSES

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Orientational relaxation of rhodamine 6G in a series of normal alcohols, ethylene glycol, chloroform and formamide has been studied using picosecond light pulses. The effects of hydrogen bonding and the structure of the liquids on the molecular rotational motion are examined.

To examine the effects of hydrogen bonding on the rotational motion of a solute molecule, the orientational relaxation times of rhodamine 6G were measured in a series of liquids covering a range of viscosities and solute–solvent and solvent–solvent hydrogen bonding interactions. Rhodamine 6G was selected for our initial studies because of its strong absorption and highly polarized transition at the laser excitation frequency and because of previous studies of its hydrogen bonding interactions [1]. The picosecond light pulse method, which was used to measure the molecular orientational relaxation times, involves the direct time measurement of the solute rotation. The principal idea of this laser technique is to induce an anisotropy in the orientational distribution of solute molecules with a picosecond excitation pulse, and to monitor the return of the system to an isotropic distribution with an attenuated picosecond pulse. Due to the induced anisotropy, the absorption of the probe pulse is polarization dependent. The decay of this dichroism with time, due to thermal molecular motions, is determined by measuring the relative transmitted intensities $I_\parallel/I_\perp$ of the probe light; $I_\parallel(t)$ and $I_\perp(t)$ are the components of the probe light polarized parallel and perpendicular to the excitation light at the time t after the excitation pulse. For rotational motion describable by the rotational diffusion equation we obtained a relation * $\ln(I_\parallel/I_\perp) \approx \exp[-(6D + 1/\tau)t]$, where D is the rotational diffusion constant and τ is the excited state lifetime. As can be seen from this relation the orientational relaxation time is given by $(6D)^{-1}$. Alternatively we can express our experimental measurements in a model independent form [3] to obtain $\ln(I_\parallel/I_\perp) \approx \langle P_2[\hat{\mu}(0)\cdot\hat{\mu}(t)]\rangle$. This corresponds to an ensemble average of a dipole correlation function where $\hat{\mu}(0)$ and $\hat{\mu}(t)$ are unit vectors along the transition dipole axis representing the dipole orientation at times $t=0$ and $t=t$ respectively and P_2 is the Legendre polynomial of degree 2.

The experimental apparatus is similar to the one described earlier [2]. A train of 1.06μ mode-locked Nd^{3+}-glass laser pulses with 8 nsec pulse separation was frequency doubled and used as the exciting source. After passing through a sample cell of 0.5 mm thickness, a small fraction of the exciting pulse was reflected back by a quarter-wave plate. This reflected beam was used as the probe beam. It has components parallel and perpendicular to the polarization of the exciting beam. The intensities of both components of the probe beam after passing through the excitation region were measured using an ITT type FW-114A photodiode and the pair of signals was displayed on a Tektronix 519 oscilloscope. The delay time between excitation and probing was determined by the round

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* For asymmetric rotor, D is a tensor and $\ln(I_\parallel/I_\perp)$ is a combination of several exponential decays whose decay constants are functions of D_1, D_2 and D_3, which are the principal diffusion constants of the molecule. The derivation of this expression, as well as the dipole correlation function, will be given in detail later.

trip time of the light pulses traveling between the sample and the quarter-wave plate. The ratio of the two components was measured as a function of delay time. The sample solutions all contained rhodamine 6G dissolved in various solvents at a concentration of 1.0×10^{-4} M/l. The viscosities of the solutions were measured using Cannon viscometers. All experiments were carried out at room temperature. The excited state lifetimes in the various solvents were obtained by excitation with the frequency doubled laser and measurement of the fluorescent decay.

It was observed that the decay of $\ln(I_{\parallel}/I_{\perp})$ was exponential in all solutions for the time range covered, namely 20 psec up to 1.6 nsec. It should be noted that the decay constant is the sum of the reciprocals of the orientational relaxation time and the excited state lifetime. The measured orientational relaxation time of rhodamine 6G and the viscosities of the various liquids are shown in fig. 1. The linear relation between the orientational relaxation time and the viscosity, as predicted by the Debye–Stokes–Einstein hydrodynamic model [4] is obeyed for the liquids up to octanol. For this model the orientational relaxation time is given by

$$\tau_{\mathrm{or}} = \eta V_m / kT ,$$

where η is the shear viscosity and V_m the hydrodynamic volume of the particle. This agreement with the hydrodynamic model is quite surprising since the hydrogen bonding interactions and the volumes of the solute–solvent complex vary considerably from chloroform to octanol. For example, rhodamine 6G hydrogen bonds more strongly with formamide than with pentanol [1] and yet has the same relaxation time in both liquids as predicted on the basis that their solution viscosities are equal. Similarly, for the chloroform and methanol systems the hydrogen bonding with rhodamine 6G is considerably different and still the relaxation times relate to the equal solution viscosities and are found to be equal. It is clear that if the rotating entity is the solute–solvent hydrogen bonded complex, then according to the hydrodynamic model τ_{or} should not scale linearly with viscosity since the volumes of the various complexes differ significantly. We find, however, that τ_{or} versus η is linear and therefore that there is no particle volume effect due to the hydrogen bonding. Similarly, the observed τ_{or} versus η linear dependence for the several liquids indicates that any effects of solvent–solvent association on the orientational relaxation times is adequately contained in the hydrodynamic description.

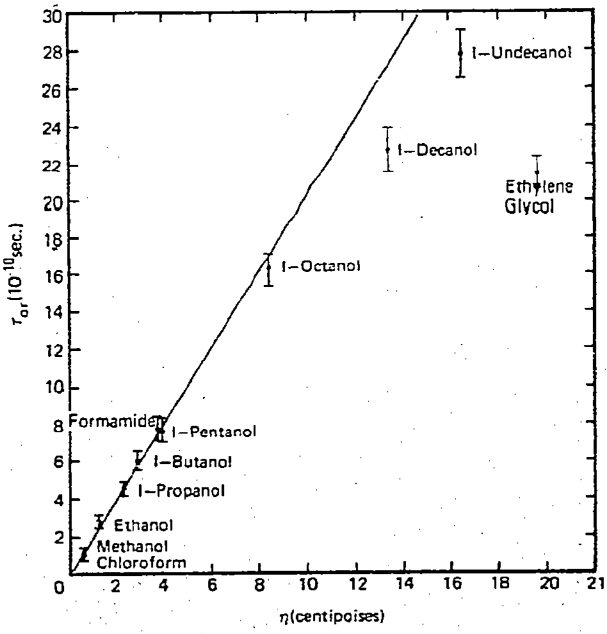

Fig. 1. τ_{or} versus solution viscosity for rhodamine 6G in various solvents.

Past studies of orientational relaxation have produced either an unclear or in some cases a contradictory description of hydrogen bonding effects on solute rotational motions. For example, McClung and Kivelson [5] found in their EPR linewidth measurements of ClO_2 in butanol that the rotational relaxation could not be described by the hydrodynamic expression. On the other hand, Angerman and Jordan [6] in EPR studies of vanadyl complexes in a series of alcohols could fit their linewidth data assuming only spin-rotational relaxation to yield rotation times varying linearly with η/T. They could not, however, explain their residual linewidth results. It is therefore not yet apparent that τ_{or} can be unambiguously obtained from EPR linewidth measurements in hydrogen bonding liquids. From dielectric relaxation measurements, Crossley [7] suggests that the longer relaxation time of chloroform in benzene versus in hexane, than expected from viscosity considerations, is due to hydrogen bonding between chloroform and benzene. However, Rothschild [8] concludes from his IR studies that there is no effect of hydrogen bonding between chloroform and benzene, on the rotational relaxation of chloroform, at least for early times. In any case, his finding of large angular rotations for chloroform indicate that the Debye–Stokes–Einstein theory for rotation is not applicable to this system.

As for the question of the insensitivity of the orientational relaxation of rhodamine 6G to its formation of hydrogen bonded complexes with the molecules of the solvent, we recognize first that the complex cannot be described as a rigid particle. If the hydrogen bond has considerable orientational freedom (≈20°), then small angular jumps of the solute would not cause a marked strain on the solute–solvent hydrogen bonding. With regard to the orientational limits of hydrogen bonding, Pimentel et al. [9] have pointed out that in many O–H...O=C systems, the hydrogen bonding is, indeed, not very sensitive to the O–H...O and C=O angle. For this case of no strong orientational preference, the effect of the bound solvent would not be notably different than the non-hydrogen bonded solvent molecules, on the rotational motion of the solute molecule. Furthermore, the complex is dynamic in that the solute–solvent hydrogen bonds are breaking and reforming* with the same or other solvent molecules and this process would also tend to reduce any strain. This description conforms with our observations that the relaxation times of rhodamine 6G in the liquids through octanol vary linearly with the solution viscosity.

The rotation of rhodamine 6G in the linear alcohols decanol and undecanol, deviates from the linear viscosity dependence as seen in fig. 1. This departure is not surprising since the solvent molecules have a greater linear dimension than the solute molecule and, therefore, the hydrodynamic model cannot be expected to be adequate. The deviation of rhodamine 6G in ethylene glycol** is felt to be due to the extensive solvent–solvent aggregation by hydrogen bonding interactions. The ethylene glycol molecule [$C_2H_4(OH)_2$] has two hydroxy groups per molecule, which can hydrogen bond with other ethylene glycol molecules of the liquid to form a polymeric network which is probably responsible for the high viscosity of the liquid, relative to the linear alcohols which have only one hydroxy group for hydrogen bonding. The rhodamine 6G does not view the full frictional effects of the polymeric structure of the solvent which are, however, contained in the value of the viscosity. These considerations of the solvent structure would be consistent with our finding that the orientational relaxation time of rhodamine 6G in ethylene glycol is considerably shorter than expected from the viscosity of the solution. Although formamide has two groups that are capable of hydrogen bonding, as does ethylene glycol, its behavior is similar to the normal alcohols. This suggests that formamide does not form the extensive network structure that we describe for ethylene glycol.

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* A description of the possible contributions of hydrogen bonding to the chemical shift and its interpretation in terms of structures and dynamics is given, for example, in ref. [10].

** The original data published by Eisenthal and Drexhage [2] for rhodamine 6G in ethylene glycol was 6.5×10^{-10} sec. Their value included the excited state lifetime and neglected the logarithmic conversion factor of 2.3. With these corrections, we find that τ_{or} is 21.3×10^{-10} sec.