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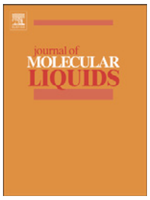

Ultrafast reaction dynamics of auramine O in a cyclodextrin nanocavity

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ABSTRACT

The effect of confinement on a barrierless ultrafast chemical reaction is investigated through the ultrafast torsional reaction of the dye Auramine O bound in a cyclodextrin (CD) inclusion complex. The rate of the barrierless reaction is inferred from the ultrafast time evolution of the fluorescence emission. The rate is decreased on formation of the complex but in a highly size dependent fashion, with only β-CD yielding a significant effect. This reflects both the formation constant for the AuO-CD complex and the nature of the confinement. Even in the case of β-CD the effect of adsorption was smaller than was observed for adsorption of the same dye at the surfactant water interface. This shows that the structure and nature of the inclusion complex and is more important in determining the degree of rate retardation than the simple fact of confinement.

1. Introduction

The dynamics of chemical reactions in molecular liquids has been studied in great detail by a combination of ultrafast spectroscopy, theory and molecular dynamics simulation [1–6]. The role of solvent friction (viscosity) in controlling the rates of activated and barrierless reactions has been thoroughly investigated [4,6]. The dynamics of charge stabilization through polar solvent reorientation (solvation dynamics) has also been the subject of numerous studies, and the role it plays in electron transfer reactions, for example, has been described [1,7,8]. More recently the methods of ultrafast reaction dynamics have been extended to investigate reactions in complex or confined media [9–13], and in some cases these have been complemented by molecular dynamics simulation [14–18]. The driving force for this new direction is the number of important chemical reactions that occur in such media. Examples include reactions in porous clays or on particulate surfaces [11], which are important in catalysis or environmental chemistry, reactions in spatially confined or structured media [19–21], such as occur in enzyme catalysed reactions in biology, or reactions in nanoconfined water [12,22,23], which is present in inverse micelles and intracellular spaces.

An important example of confined media is provided by the cyclodextrins (CDs) [24]. These comprise oligosaccharide molecules arranged in a ring to form a toroidal cavity. The number of saccharide units determines the size of the cavity. The interior of the cavity is relatively hydrophobic while the exterior is hydrophilic. As a consequence of this structure CDs can form inclusion complexes where they act as host to guest molecules which are wholly or partly included into the cavity. Such guest molecules might not otherwise be soluble or stable in aqueous solutions. This has led to CDs being employed as drug delivery vehicles. In addition the restricted geometry and amphiphilic character of CDs makes them useful models of enzyme active sites [25].

As a result of this importance, their ease of preparation and the possibility of tuning the size of the cavity through variation of the number of saccharide monomers, CDs have been widely employed as confining media for a number of excited state reactions including proton transfer [26], solvation dynamics [21] and, of most relevance to the present study, intramolecular structural reorganisation. Early work in this area was reviewed by Douhal in 2004 [27]. Since then there have been a number of studies of excited state structural dynamics in CDs including: cis-trans isomerisation of an azo dye; [28] isomerisation of a synthetic model of the photoactive yellow protein chromophore; [29] isomerisation in retinal; [30] intramolecular torsional dynamics in the fibril sensor thioflavin T [31].

In this work we investigate the effect of formation of an inclusion complex with CD on the excited state torsional motion of the dye molecule Auramine O (AuO). AuO has been studied in detail in molecular liquids [32–35]. The fluorescence quantum yield was shown to be a linear function of the solvent viscosity. This was ascribed to an excited state relaxation involving torsional motion of the phenyl rings leading to a crossing with the ground state surface, causing fluorescence quenching by internal conversion [35]. Subsequent transient absorption experiments showed that the initial relaxation was in fact to a dark excited state conformation of twisted charge transfer (CT) character, which decayed on a slower timescale to the ground state [32]. Consequently the fluorescence decay was observed to be faster than the ground state recovery. Glasbeek et al. modelled the excited state dynamics of AuO (measured through its time resolved emission spectrum) as a barrierless diffusive motion of the phenyl rings on an excited state surface formed through coupling of an emissive locally excited state and a dark CT state [34]. The relaxed excited state then reverts to the ground state through internal conversion. Although the diffusive

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model was very successful in alcohol solvents an extension to a range of solvents indicated a correlation between the excited state decay time and the polar solvation dynamics, one consequence of which was a faster than expected decay time in water compared to other fluid polar solvents [23].

The viscosity dependent dynamics of AuO is so well characterised that it has been used as a probe of reactive dynamics in complex media. Two groups investigated the excited state relaxation of AuO in nanoconfined water droplets in inverse micelles [12,22,23,36–38]. The effect of confinement was to slow the rate markedly, an effect which could be ascribed to slower torsional motion of AuO due to enhanced local friction, particularly reflecting the interfacial friction. The excited state dynamics were modelled as diffusion on a barrierless surface, and the nature of the friction in the confined environment of the micelle was analysed, and found to be more complex than in molecular liquids [12]. More recently AuO was used as a probe of reactive dynamics in ionic liquids [39–41]. These measurements utilized a novel multidimensional electronic spectroscopy, which confirmed and refined the picture of AuO relaxation from linear transient spectroscopy but also identified a new slowly relaxing channel. It was also found that the highly dispersed distribution of relaxation times of AuO in the ionic liquid could be analysed in terms of a distribution of effective barrier heights in the very slowly relaxing ionic environment.

In the following the excited state dynamics of AuO in CD solutions as a function of the cavity size and CD concentration are investigated. In the restricted CD environment the dynamics are shown to be slowed down significantly compared to aqueous solution, but in a size selective fashion. The origin of this behaviour is discussed.

2. Experimental

Time resolved fluorescence was measured with an up-conversion spectrometer described in detail elsewhere [12]. The laser was a mode locked titanium sapphire delivering 15 fs pulses at a 76 MHz repetition rate at a fundamental wavelength of about 820 nm. The fluorescence up-conversion technique is essentially an ultrafast sampling method in which the fluorescence excited by an ultrafast pump pulse (second harmonic of the fundamental at 410 nm) is sampled by sum-frequency generation in a nonlinear crystal in which the fluorescence is mixed with the residual ultrafast fundamental pulses. The sum frequency intensity is proportional to the instantaneous fluorescence intensity, which is measured by a photon counter and recorded as a function of the delay between pump and sampling pulse. By minimising dispersive optical elements and carefully balancing group velocity dispersion a time resolution of better than 50 fs is possible. In the present experiments additional glass filters were employed to remove scattered light which degraded the resolution to 70 fs.

For sample preparation the glucose and α-, β- and γ-cyclodextrins were obtained from Sigma-Aldrich (purity >98%). CD concentrations were up to 13 mM in triply distilled water. The glucose concentrations were seven times higher. AuO was also obtained from Sigma-Aldich as the monohydrochloride with >80% impurity; it was established that none of the impurities contribute to the fluorescence. The AuO concentration was typically 0.1 mM. Specifically for AuO in β-CD a slow decolorization was observed so only freshly prepared samples were investigated.

The fluorescence up-conversion data were fitted to a multi-exponential function as described elsewhere [12]. Finally the mean fluorescence lifetime is calculated from the exponential decay terms according to the equation: $\langle\tau\rangle = \sum A_i\tau_i / \sum A_i$.

3. Results and Discussion

The absorption spectra of aqueous solutions of AuO in the presence of α-, β-, and γ-CD (13.2 mM) or an equivalent concentration of glucose (0.09 M) are shown in Fig. 1a. Neither α-CD nor glucose gave

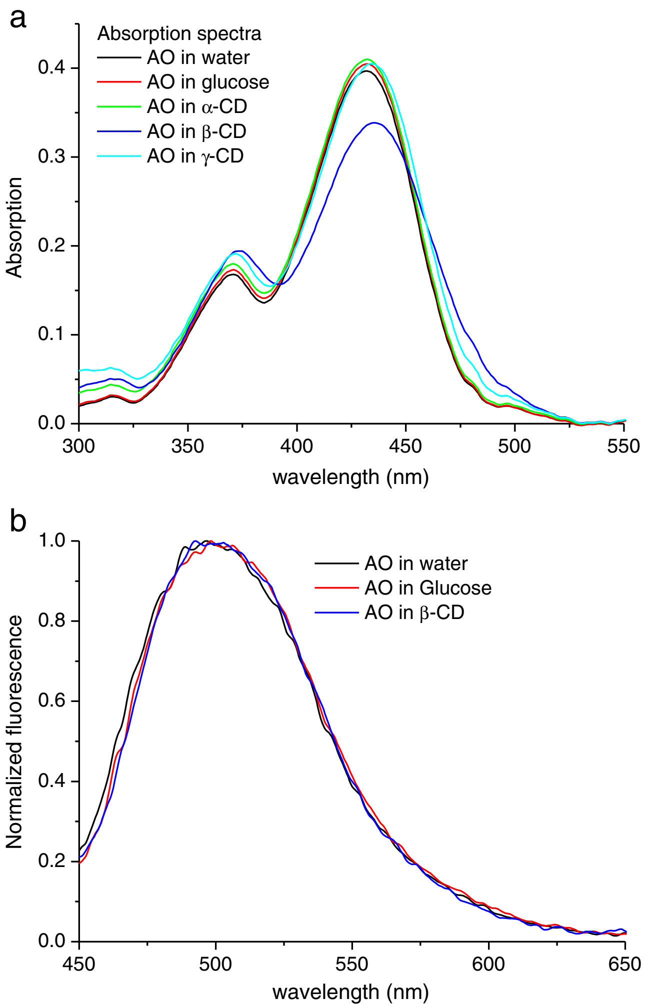

Fig. 1. (a) Electronic absorption spectra of AuO in aqueous solutions with CDs and glucose. (b) Fluorescence spectra for three aqueous solutions. Note that the fluorescence spectra are obtained after subtraction of a substantial Raman background, so the profile is only qualitatively accurate.

rise to any change in the AuO absorption spectrum compared to the aqueous solution. The β-CD causes a significant broadening and shift of the AuO spectrum towards longer wavelength. In γ-CD similar changes in the spectrum are observed but the effect is much less marked than for β-CD. Studies of the AuO spectrum as a function of CD concentration showed that the spectral changes were complete in β-CD at a concentration of 6 mM, while for γ-CD the shift continues to develop until at least 13 mM. The distinct character of the AuO/β-CD solution was further illustrated by the observation that this solution only was observed to decolorize over a period of days. Similar behaviour was observed for AuO in the small inverse micelles stabilized by the non-ionic surfactant igepal. This was assigned to slow deprotonation of the coloured anionic AuO to generate the UV absorbing neutral form. Deprotonation is favoured when the cationic form is incompletely hydrated.

The fluorescence emission of AuO in aqueous solution (Fig. 1b) is weak and somewhat distorted by Raman scattering from the solvent. This very low quantum yield precludes determination of the binding constant, even for the β-CD solution. However, the emission data do show that there is no large change in the emission spectrum in the presence of β-CD and no dramatic changes in intensity as a function of CD concentration. However, in the case of very weak emission the time resolved fluorescence is often more informative. Fluorescence up-conversion data were measured at 490 nm (approximately