Chemical reaction dynamics of some simple molecules in solution

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Chemical reaction dynamics of some simple molecules in solution

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Solvent is a critical component of reactive processes occurring in solutions. Examples of solvent effects in charge shifting ($ClO^- \rightarrow Cl^-O$), vibration–rotation interactions (HgI) and geminate dynamics following disulphide bond dissociation are described.

Keywords: chemical reaction dynamics; cage dynamics; vibration–rotation coupling; impulsive dissociation; charge switching

1. Introduction

It is well known that reactive processes involving relaxation, such as electron transfer, atom transfer and conformational dynamics in the condensed phases, are critically dependent upon the *nuclear motions* of the atoms that sense the chemical change. These nuclear motions involve both internal modes and modes of the surrounding medium. Their time scales can range over many orders of magnitude depending on whether they are inertial-like, simple local rearrangements, or more complex structural changes involving the motions of many atoms over a significant spatial region. It is therefore important to carry out experiments on the dielectric responses over this whole range of time scales in order to fully understand the basis of the dynamics.

In the past few years there was a considerable expansion of interest in solvation dynamics (Barbara & Jarzeba 1990; Cong *et al.* 1995; Jimenez *et al.* 1994; Rossky & Simon 1994) and its relationship to theory (Kumar & Maroncelli 1995; Maroncelli 1991; Maroncelli & Fleming 1988). In order to make connections with theory the notion of linear response has often been used. In the linear response approach it is conjectured that the parameters of the dynamics, which are generally correlation functions of the various dynamical variables, are entirely determined by the *fluctuations* occurring in the equilibrium distribution (Chandler 1990). Thus, this theory would claim the ability to predict the detailed response to *small* perturbations solely on the basis of information derived from their *equilibrium fluctuations*. The validity of this approach, and how a small perturbation is defined, has often been tested by simulations (Fonseca & Ladanyi 1991; Phelps *et al.* 1993). Although the theory can evaluate itself, for example by means of non-equilibrium calculations, it will be important to have experimental measurements that explicitly address this issue. In the work presented here we are seeking a microscopic description of the dielectric response of simple liquids like water through studies of the photoproper-

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ties of small molecules and ions (Gnanakaran *et al.* 1996). In particular, the charge shifting of ClO^- is described with the emphasis on obtaining a molecular picture of solvation dynamics. The experiments are supplemented with classical molecular dynamics simulations from which the relevant correlation functions are calculated and used to assess the assumptions of linear response theory.

By using polarized light in time resolved experiments a more detailed picture of the dynamics of chemical reactions in solution can be obtained. The time dependence of the *anisotropy*, which is proportional to the difference between the signals with pump and probe pulses polarized parallel and perpendicular to one another, is obtained in these experiments. It permits the determination of the symmetry characteristics of transitions, which in turn helps to establish the nature of the electronic states involved in the reaction. It can also enable the detection of coherence and the measurement of coherence loss (Wynne & Hochstrasser 1993). The rotations of the transition dipoles associated with the reactant, the transition states and the products of the reaction can also be determined (Hochstrasser *et al.* 1991). In addition, the anisotropy can help unravel the complex kinetic behaviour that can arise from overlapping signals of different species that are involved in a reaction (Cross *et al.* 1983; Sension *et al.* 1993). In the solution phase, anisotropy measurements have enabled the study of excited state energy transfer between identical chromophores (Kim *et al.* 1989; Zhu *et al.* 1993), the dynamics and energy transfer within proteins (Haran *et al.* 1996), the alignment of reactant and product states (Sension *et al.* 1993), and the angular effects of the coupling of internal and overall motions of molecules (Raftery *et al.* 1993; Sension *et al.* 1993). In the present work anisotropy measurements are applied to the impulsive photochemical dissociation fo HgI_2 which generates iodine atoms and HgI molecules. The emphasis of the present work is to describe the influence of solvent on the nearly inertial motions occurring at early times, at time scales much shorter than the conventional rotational diffusion, but comparable with the vibrational period. This is the regime where vibrational–rotational coupling becomes evident in time domain experiments. Molecular dynamics simulations again prove useful in finding detailed interpretations of measurements.

The third example involves cage dynamics. The concept of cage dynamics in bimolecular reactions arose from the early pioneering experimental work and theoretical simulations of Rabinowitch (Franck & Rabinowitch 1934; Rabinowitch & Wood 1936). The coherently produced fragments of photodissociation reactions in solutions may have relative kinetic energy that is large enough that the fragments may separate by pushing the surrounding solvent molecules aside. In this case the distance between fragments will gradually increase until the imparted translational motion is thermalized and diffusion begins. Caging occurs when the force exerted by the nascent fragments on the solvent molecules is not so large. In some cases the solvent may be able to dissipate the excess kinetic energy and then exert a force opposed to the initial motion so that the reflected trajectories may result in recombination. In such situations the solvent is essentially impulsively excited by the photodissociation processes and for a time one can imagine all the solvent–solute configurations in the ensemble might move synchronously. Relevant to this question are the early experimental studies of the photodissociation of CH_2I_2 into I and CH_2I (Schwartz *et al.* 1993) which demonstrated a 230 fs geminate recombination component in a number of solvents, that was interpreted to result from single collisions of the fragments with the solvent cages. The recent studies of iodine in argon by Apkarian and co-workers (Li *et al.* 1995; Zadoyan *et al.* 1994) and Zewail and co-workers (Liu *et al.* 1993;

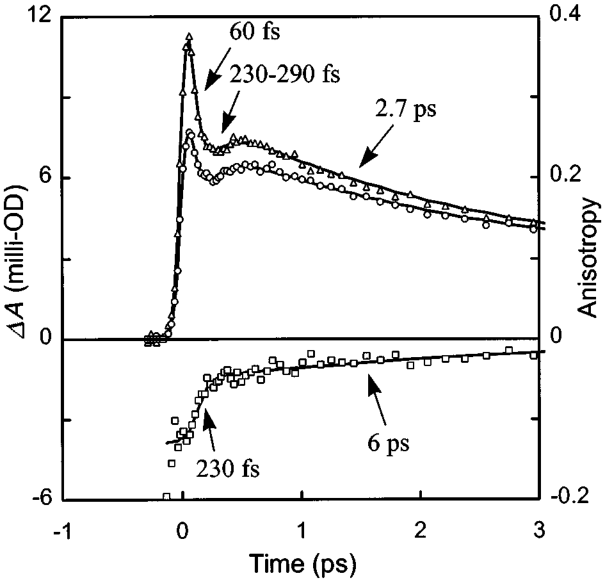

Figure 1. A representative transient absorption and anisotropy probed at 440 nm after 320 nm photolysis of ClO^- in water. Probe wavelength dependent transients and their anisotropies were obtained between 490 nm and 380 nm. The solid lines and time constants are fits using global parameters for optimizing all the transients obtained simultaneously (see Lim *et al.* 1997 for details). The anisotropy measurement establishes the presence of the diatomic molecule. The symbols are data (open triangles, open circles and open squares are $\Delta A^{\perp}$, $\Delta A^{\parallel}$ and anisotropy, respectively). The left (right) ordinate is for the upper (lower) panel.

Wan *et al.* 1997; Wang *et al.* 1995) also show clearly the effects of the oscillatory forces exerted by solvent molecules on the coherent motion of the iodine atoms. It is interesting to conjecture whether such concerted solvent responses could ever prevail in complex room temperature liquids such as water and organic solvents. In all of these experiments the wavepacket dynamics or the populations of the undissociated or reassociated states is measured. To see more directly the full solvent coherent motion, the fragments or the solvents should be studied directly, since only a fraction of the concerted solvent assisted motions might lead to geminate recombination. This is the situation with the disulphide dissociation reactions discussed below. For these examples the anisotropy again proved to be invaluable in exposing the motions of interest.

2. Charge switching, solvation and the linear response

The experiments on ClO^- invlove excitation at *ca.* 300 nm followed by probing in the range of 400 nm (Lim *et al.* 1997). The results show changes occurring on three time scales. There is a very fast (*ca.* 60 fs) process which is a spectral shift, followed by an intermediate time process of *ca.* 250 fs. The slower processes on the time scale of a few ps are interpreted as vibrational relaxation in the ground state of ClO^-. All of these steps are evident in the typical result shown in figure 1. The intermediate step includes the formation of Cl atoms which are identified by their spectrum and the back electron transfer process to the ground state both of which appear to be controlled by solvent dynamics.

The equilibrium simulations of ClO^- in water yield the radial distribution function

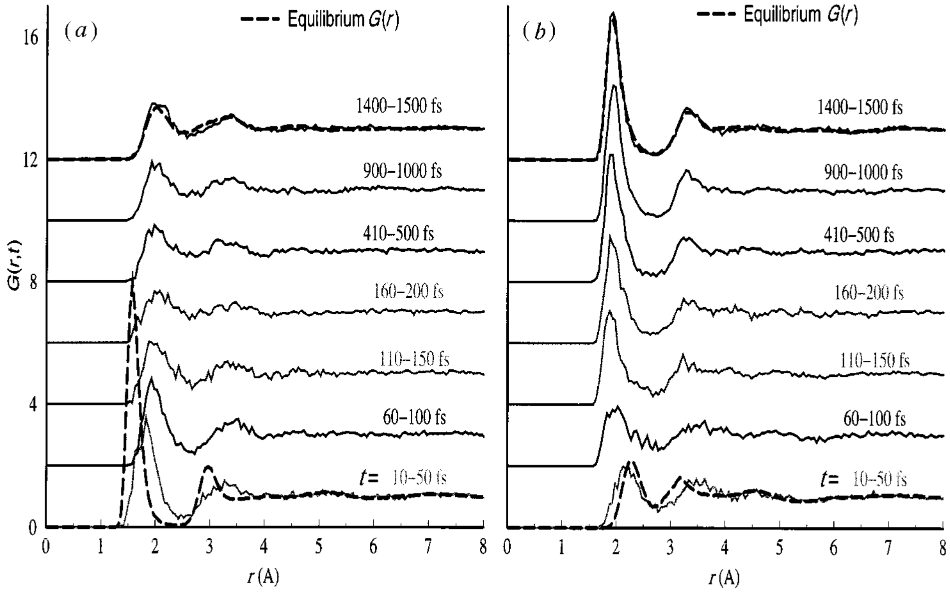

Figure 2. Time-dependent radial distribution function ($G(r,t)$) for the charge shifting of $ClO^- \rightarrow Cl^-O$ in H_2O. (*a*) $G(r,t)$ for oxygen of $[ClO]^-$ and hydrogen of H_2O. (*b*) $G(r,t)$ for chlorine of $[ClO]^-$ and hydrogen of H_2O. Dashed lines at the top and bottom of each of the sets show the equilibrium radial distribution functions of ClO^- and Cl^-O respectively.

$G(r)$, for H and O atoms of solvent around oxygen and chlorine. In the ground state the oxygen has most of the extra charge and accordingly there is a relatively well-defined average structure of solvent molecules around it. ON the contrary, the solvent structure around neutral Cl is not so well ordered. On suddenly switching the charge from O^- to Cl, such as occurs in the actual experiment following light absorption, the non-equilibrium simulation trajectory was obtained and used to calculate $G(r,t)$ for each time t after charge switching at $t=0$. The $G(r)$ and the time dependent $G(r,t)$ for Cl^- and O of the excited state are shown in figure 2. There are two dominant time scales in the results. The first, 60 fs, clearly corresponds to the dissociation of the water molecules around the oxygen. This begins immediately when the O–H_2O bonds are severed by the charge switch. However, the calculation shows that the solvent structure around Cl^- does not form immediately but it takes the $G(r,t)$ about 300 fs to become nearly the same as the equilibrium $G(r)$ for the Cl^-O structure. We consider it likely that the two time scales seen in $G(r,t)$ are associated with the two experimentally observed times. The fast dissociation of a well-defined structure from oxygen and slower reorganization of more randomly distributed solvent into a structure around chlorine is reasonable on entropic grounds. It is obvious that this picture, at least in skeleton form, is likely to be transferable to other strongly solvated systems. The dissociation part will correspond to the inertial response which in the present case has a very clear physical interpretation. The simulation shows that translational and rotational motions of water are involved in this fast motion.

We also examined the applicability of linear response theory. The ($ClO^- \rightarrow Cl^-O$) system is asymmetric in as much as the average solvent structures around the two forms are not interchangeable by symmetry, as would be the case, say, for the $Fe^{+2} \leftrightarrow Fe^{+3}$ system (Bader & Chandler 1989; Kuharski *et al.* 1988). The classical distribution of energies associated with the transitions from the equilibrium state of ClO^- to Cl^-O was used to compute the free energy curves along the solvent coordinate using known methods (Carter & Hynes 1989, 1991; Hwang & Warshel 1987; Hynes 1986). The potentials for ClO^- and Cl^-O are not the same although they are both harmonic, indicating that there is some (*ca.* 20%) nonlinearity in the dynamics.

3. Solvent effects on the vibration–rotation interaction of HgI (Volk *et al*. 1997*a*)

In impulsive photolysis of linear HgI_2 which was studied in the gas phase (Baumert *et al.* 1993; Bowman *et al.* 1989; Dantus *et al.* 1989*a*, *b*; Gruebele *et al.* 1990; Pedersen *et al.* 1993) and more recently in solutions (Pugliano *et al.* 1993, 1995, 1996), the excitation by a polarized light pulse occurs via transition moments that are either parallel or perpendicular to the bond axis. The ground state of HgI_2 is $^1\Sigma$ and the lowest energy absorption band in solution consists of transitions to both $^1\Sigma$ and $^1\Pi$ states (Pugliano *et al.* 1995). The photoreaction leads to the $(X)^2\Sigma$ state of HgI and both ground and excited states of the I atom. The reactive motion takes about 90 fs in solution, which corresonds to just less than one-half of a vibrational period. As the molecule dissociates the electronic wavefunctions change, and this was seen in the anisotropy due to the rotation of the transition moment in the molecular frame (Volk *et al.* 1997*a*). The anisotropy is sensitive to the presence of electronic coherence introduced by the excitation of degenerate Π states, or superpositions of Π and Σ states (Wynne & Hochstrasser 1993, 1995). While the products of the reaction, HgI and I, are forming, their transitions can be probed. This experiment yielded information regarding the alignment of the transition moments of the product and the reactant molecules. Misalignments arise from torques associated with the reactive motion, from the coupling of the internal and external motion, and from the equilibrium inertial angular motion of HgI modified by the fluctuating torques exerted by the solvent molecules. These fluctuating torques give rise to the rotational diffusion of HgI.

The rotational dynamics of diatomic molecules in solutions has been studied theoretically and experimentally (Burshtein & Temkin 1994). The experiments were mainly carried out in the frequency domain by means of dynamic light scattering, polarized Raman line shapes or by means of magnetic resonance (Berne & Pecora 1976; Evans *et al.* 1982; Gordon 1965*a*; Steele 1969, 1976). Recently, a time domain experiment on I_2^- has been reported (Banin *et al.* 1993; Banin & Ruhman 1993). The characteristic time constant, τ_c for loss of rotational coherence from an ensemble of rotors at temperature T is given by $(2\pi/9)(I/k_BT)^{1/2}$, where I is the moment of inertia. For HgI at 300 K the value of τ_c is 1.05 ps. The line shapes of polarized Raman transitions of diatomic molecules frequently indicate that this inertial component contributes significantly to the decay of the anisotropy (Gordon 1965*b*, *c*, 1966). It is usually followed by a slower diffusive component (Debye 1928). Several models have been proposed to describe the anisotropy decay for systems which evolve from free rotation at short times to rotational diffusion at long times (Chandler 1974; Fixman & Rider 1969; Gordon 1966; Kivelson & Keyes 1972; Lindenberg & Cukier 1975; Lynden-Bell & McDonald 1982; Steele 1963*a*, *b*, 1976). Therefore the anisotropy can be used to examine the angular motion as the nuclei move through the transition state and the rotational energy distribution of a reaction, if the time resolution is faster than rotational energy relaxation. The interpretation of such experiments can be greatly aided by simulations of the classical dynamics.

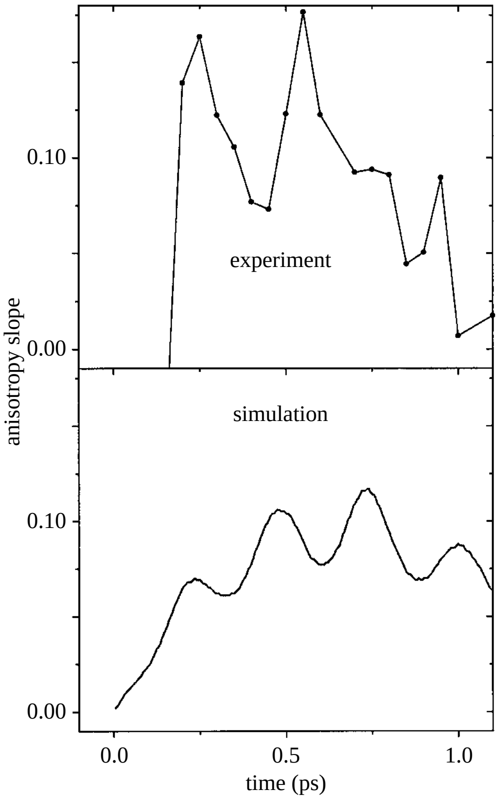

Figure 3. Slope of the anisotropy decay determined from the experiment (top) and non-equilibrium MD simulation of HgI with excess vibrational kinetic energy of 1000 cm^{-1} starting from the equilibrium inter-atomic distance in ethanol (bottom).

The vibration–rotation coupling is observed as an oscillatory component on the early part of the anisotropy decay of HgI probed at 490 nm. These oscillations correlate with the motion of the HgI wavepacket. This effect corresponds to an oscillatory motion of the transition dipole vector in the laboratory frame. The instantaneous slope of the experimental anisotropy decay function is shown in figure 3(top), which makes clearer the origin of the oscillations: the slope is systematically lowest when the molecule is most extended, corresponding to the maxima of the transient absorption oscillations (Pugliano *et al.* 1995, 1996), and largest when the molecule is compressed. In the time regime of the first 500 fs the nature of the reorientation dynamics is not well defined, being neither inertial nor classically diffusive. As the wavepacket moves from the repulsive to the attractive side of the potential, both the moment of inertial and the hydrodynamic volume will increase and slow down the molecular reorientation. At the 490 nm probe wavelength the observed HgI molecules at the centre of the distribution are stretching from about 2.65 to 3.2 Å (Pugliano *et al.* 1996). The hydrodynamic length of HgI is 6.43 Å, so the wavepacket motion of a diffuser would give rise to an 8.5% peak-to-peak oscillation in the molecular volume. Since the rotational diffusion time is generally proportional to volume (Berne & Pecora 1976), this would result in an oscillation in the slope of the anisotropy decay of about the same magnitude. Such a modulation is somewhat smaller than but consistent with the experiment, given the signal to noise. The inertial part of this effect is the time

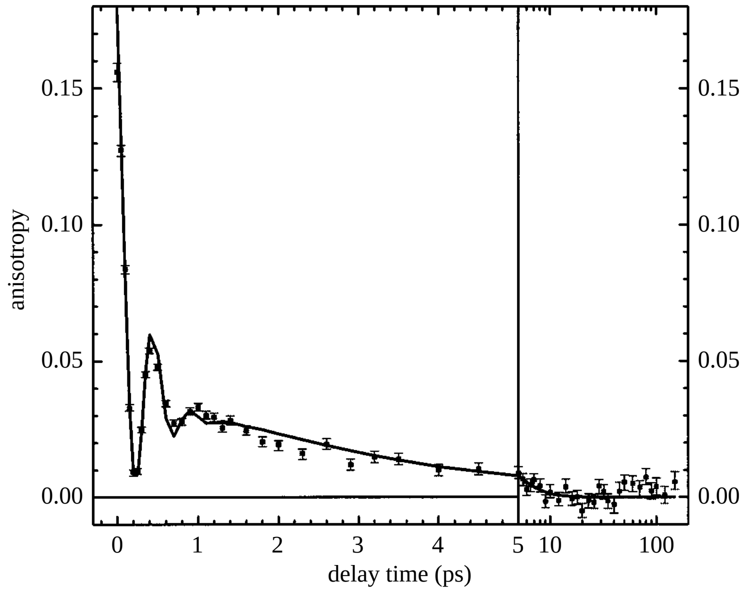

Figure 4. Anisotropy decay of the thiyl radical absorption in TIPDS after photodissociation. The solid line is a fit of the parallel and perpendicular transient absorption to the model discussed in the text. (This fit showed that magic angle data are well described by one rising exponential (0.12 ps) and a double exponential decay (0.85 ps and 24.1 ps).) The best fit parameters are: effective frequency of the oscillations, $\beta_1 = 74.3\ \mathrm{cm}^{-1}$; frictional parameter, $\beta/\beta_1 \sim 10^{-3}$; rotational diffusion coefficients, $D_\perp = 0.06\ \mathrm{ps}^{-1}$ and $D_\parallel = 0.62\ \mathrm{ps}^{-1}$; initial displacement, $\gamma_0 = 63°$.

domain manifestation of the non-rigid rotor character of the HgI. We calculated the inertial rotational coherence decay of HgI treated as a free anharmonic non-rigid rotor and found oscillations in the slope of about the same as those estimated for diffusion. These results, from a non-equilibrium molecular dynamics simulation, are shown in figure 3(bottom). The agreement is not perfect but the qualitative features are reproduced. To the best of our knowledge a wavepacket characteristic of this sort was not previously reported for a diffusing molecule. This analysis can be used to establish bond length variations as contraction or expansion in systems where the potential functions for ground and excited states are not known. With small molecules the peaks in wavepacket signals occur when the Franck–Condon factors maximize during the oscillation. These results confirm that in HgI the peaks correspond to HgI molecules at the attractive wall of the potential. The inertial contribution to the signal can be calculated exactly so it should be possible by means of this technique to examine non-adiabatic solvent effects on the internal motions of the nuclei. Obviously, in order that this effect be observable the molecule must rotate during a vibrational period by enough to change the anisotropy, so that the largest changes will be seen with very low frequency modes.

4. The anisotropy of the impulsive dissociation of disulphides

The photodissociation of many aromatic disulphides into arylthiyl radicals has been studied by using ultrafast spectroscopic methods and geminate recombination was reported in some cases (Autrey *et al.* 1995; Borisevich *et al.* 1990, 1992; Bultmann

& Ernsting 1996; Ernsting 1993; Hirata *et al.* 1997; Nakamura *et al.* 1980; Scott & Liu 1989). As a preliminary to our recent studies of disulphide bond cleavage in model peptides (Lu *et al.* 1997; Volk *et al.* 1997*b*) we carried out femtosecond measurements on a number of aromatic disulphides. In addition to conventional pump/probe experiments we measured the *anisotropies* associated with probing the transient absorption of the thiyl radical fragments. It is this experiment that is focused on in this paper since it permits visualization of the coherent solvent responses that are not coupled to the geminate recombination process.

Experiments on the impulsive release of thiyl radicals from disulphides by photodissociation show that the anisotropy of the transient absorption exhibits oscillations. These oscillations are not easily seen in the isotropic absorption signal. However, the magnitudes of the oscillations in the anisotropy is such that rather large angular motions would need to be involved. This effect is seen in several alkyl-substituted diphenyldisulphides and all show comparable effects. The most oscillatory anisotropy (i.e. the least damped motion) was found for triisopropyldiphenyldisulphide (TIPDS) the results for which are shown in figure 4.

The possible interpretation of these anisotropy results is to relax the constraint, usually employed for rigid molecules, that the pumped and probed transition dipole moments are fixed in the frame of the rotating radical fragment. Instead we explore the idea that the probed dipole corresponding on average to the direction of the C–S bond, undergoes internal motions relative to the principal axes of the rotational diffusion tensor of the thiyl radical. To find an analytic result one needs to assume that the overall and the free internal motions are independent, in which case the effect of the overall diffusion becomes a separable contribution to the anisotropy decay. For a cylindrical diffuser with rotational diffusion coefficients $D_\parallel$ and $D_\perp$ the anisotropy for such a situation takes the following form (Szabo 1984):

$$r(t) = 0.4 \sum_{a,n} \exp\{-[6D_\perp + a^2(D_\parallel - D_\perp]t\}[d_{an}(\theta)]^2 d_{n0}(\theta_{\mathrm{A}}) d_{n0}(\theta_{\mathrm{P}}) \cos n\phi_{\mathrm{AP}} \mathit{\Gamma}_{nn}(t), \tag{4.1}$$

where the factor $\mathit{\Gamma}_{nn}(t)$ describes the under-damped internal motion that is giving rise to the oscillations in the signal; the $d_{ij}(\theta)$ are the polar parts of the Wigner rotation matrices *of rank two* tabulated in the literature (Brink & Satchler 1979); the angle between the axis of internal motion (this axis is designated as Z) and the unique axis ($\parallel$) of the diffusing cylinder is θ; θ_{A} and θ_{P} are the polar angles between Z and the absorbing (A) and probed (P) transition dipoles respectively; and ϕ_{AP} is the azimuthal angle between these dipoles projected onto the plane perpendicular to Z.

The dynamics and frictional damping of any internal motions about Z were described by a Langevin equation for a damped harmonic oscillator in the presence of a fluctuating force. If harmonic angular motion on a potential $V = 1/2I\omega^2\gamma^2$ is assumed, with I being the moment of inertial and ω the fundamental frequency, the Green's function $W(\gamma, t; \gamma_0 u_0)$ describing the probability that the angular displacement will be γ at time t, given that it was γ_0 and that the velocity was u_0 at time $t = 0$, is well known (Chandrasekhar 1943). The velocity averaged correlation function $\mathit{\Gamma}_{nn}(t)$ describing the evolution is then given by

$$\mathit{\Gamma}_{nn}(\gamma_0, t) = \int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}n\gamma} W(\gamma, t; \gamma_0) \mathrm{e}^{\mathrm{i}n\gamma_0} \, \mathrm{d}\gamma, \tag{4.2}$$

where $W(\gamma, t; \gamma_0)$ is the probability of the angle being γ at time t assuming a delta function distribution of initial angles centred at γ_0 and a Maxwell–Boltzman distribution of initial velocities. After evaluation of the correlation functions the final general expression for the anisotropy is

$$r(t) = 0.4 \sum_{a,n} \exp\{-[6D_\perp + a^2(D_\parallel - D_\perp]t\}[d_{an}(\theta)]^2 d_{n0}(\theta_\mathrm{A}) d_{n0}(\theta_\mathrm{P}) \cos n\phi_\mathrm{AP}$$
$$\times \exp[-(1 - L^2)(n^2 v^2/2 + \mathrm{i}n\gamma_0)], \tag{4.3}$$

where v^2 is the mean squared angular velocity in the equilibrium distribution and $L = L(t)$ is given by

$$L(t) = \exp[-\beta t/2](\cos \beta_1 t/2 + (\beta/\beta_1) \sin \beta_1 t/2). \tag{4.4}$$

The friction is β (i.e. $u\beta$ is the frictional force) and the effective frequency of the oscillations is $\beta_1 = (4\omega^2 - \beta^2)^{1/2}$. Specializing to the case of the thiyl radicals, we modelled the free internal motion as a rotation about an axis perpendicular to the C–S bond. The absence of significant oscillations on the isotropic signal indicates that the motion giving rise to the oscillations is not dominantly along the reaction coordinate for geminate recombination. Figure 4 shows a fit of the data for TIPDS to equation (4.3) using a multidimensional fitting program. The results exhibit the proper form but the angles are unphysically large. Reasonable fits were also obtained for other examples by using the same equation (Volk *et al.* 1997*c*).

The model is intended to describe the time dependence of the anisotropy from an ensemble of thiyl radicals that are generated in a highly non-equilibrium state and which recover to equilibrium under the influence of a harmonic force. What is predicted is a rotation of the electronic transition dipole moment. Unfortunately the measurements do not assign the precise microscopic origin of the motion. We are considering two possibilities. In one, the reactive force generates a radical solvent complex that is greatly displaced along the solvent coordinate and the recovery is a periodic solvent motion. Another possibility being considered is that the side chains in the nascent radicals are significantly displaced from their equilibrium configurations and that their rotational motion induces an overall rotation of the electronic transition dipole in the laboratory frame. Finally, it is necessary to incorporate the coupling between internal and overall motions to obtain a complete picture of the dynamics.

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