J-Coherence and Keilson−Storer Models: Applications to the Femtosecond Dynamics of Orientational Relaxation

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The interrelationship between the J-coherence and the Keilson−Storer models of orientational relaxation is established, and the validity of the Langevin description in reproducing the real time measurements of the anisotropy decay is discussed.

In their fascinating paper,[1] Zewail and co-workers presented the results of the real time measurements of the orientational relaxation (OR) of iodine molecules in the noble gas solvents under a broad scale of densities, ranging from a dilute gas to liquid (see also ref 2 for a concise version of ref 1). In connection with this, I would like to comment on the following major points.

Zewail and co-workers emphasize the necessity to take into account the effectiveness of intermolecular collisions in transferring angular momentum. To describe the influence of this effect on the OR of diatomic molecules in an atomic solvent, they developed the J-coherence model.[1,2] The essence of this model is as follows. A solute−solvent collision is treated as an instantaneous encounter of two rigid bodies: a molecule is mimicked by two overlapping smooth spheres, and an atom is represented by a smooth sphere of different radius. The Poisson collision statistics, random distribution of impact parameters, and geometry of the collision partners is simulated and a trajectory of an individual molecule is calculated. Various correlation functions (CFs) are obtained by averaging over a large number (of about 100 000) trajectories. An approach somewhat akin to that developed by Zewail and co-workers was also worked out for the description of OR of symmetric top molecules.[3] So, a practical implementation of the J-coherence model requires a substantial amount of computer calculation. However, there exists a very similar in spirit, but far more mathematically simple, model of the OR, viz. the Keilson−Storer (KS) model.[4−7] The underlying assumptions and predictions for this model have been discussed in the literature.[4−7] Note that the rotational motion in the KS model is governed by the two parameters: z_c, which is the collision frequency, and $-1 \le \gamma \le 1$, which is the collision strength. When the pump and probe dipole moments are parallel to the axis of a linear molecule, the anisotropy of molecular emission, $r(t)$, is proportional to the second rank orientational CF (OCF): $r(t) = 2/5\, G_{00}^2(t)$. The KS model allows one to calculate the Fourier-spectrum of this OCF through the simple three term recurrence relations:[7]

$$\tilde{G}_{00}^2(\omega) \equiv \int_0^\infty \mathrm{dt}\, \exp\{-i\omega t\} G_{00}^2(t) = (1 + 2b_0)/i\omega \quad (1)$$

$$\frac{16(m+2)}{\sigma_{m+1}} b_{m+1} - \left\{ \frac{8m+10}{\sigma_{m+1}} + \frac{8m+6}{\sigma_m} + \zeta_m \right\} b_m + \frac{4m}{\sigma_m} b_{m-1} = \frac{3}{i\omega} \delta_{m0} \quad (2)$$

Here

$$\sigma_m \equiv i\omega + z_c(1 - \gamma^{2m}),\ \zeta_m \equiv i\omega + z_c(1 - \gamma^{2m+1}) \quad (3)$$

The KS model contains, as a special case, the J-diffusion model ($\gamma = 0$) and the rotational Fokker−Planck equation (FPE) ($z_c \to \infty$, $\gamma \to 1$, $z_c(1-\gamma) \to \nu_J = \text{const}$).[4−7] In this latter case

$$\sigma_m \to i\omega + 2m\nu_J,\ \zeta_m \to i\omega + (2m+1)\nu_J \quad (3')$$

The fact that the angular momentum transfer due to a collision depends on the collision strength immediately leads one to the conclusion that the intercollision time, $\tau_c = 1/z_c$, and the angular momentum relaxation time, τ_J, differ from each other. If the solvent density is not very high, both of these quantities can be calculated within the Enskog approximation.[8] In the case of nonspherical molecules, the so obtained expressions for τ_c and τ_J are somewhat complicated and require numerical integration.[1,8] However, by invoking the simplified version of the Enskog theory, one can calculate the ratio ν_J/z_c by the formula[9]

$$\frac{\nu_J}{z_c} = \frac{\langle \vec{J} \Delta \vec{J} \rangle}{\langle \vec{J}^2 \rangle} \quad (4)$$

Here $\nu_J \equiv \tau_J^{-1}$ is the angular momentum relaxation frequency, and $\Delta\vec{J}$ is the angular momentum change due to a single collision. Equation 4 allows one to establish the interrelationship between the J-coherence and the KS models. Indeed, Zewail and co-workers derived the explicit formula for $\Delta\vec{J}$ in their collision model (ref 1, eq 20). By inserting this expression into eq 4 and performing all the necessary averagings, one arrives at a remarkably simple result

$$\frac{\nu_J}{z_c} = 2 - \frac{a^2 - 1}{a} \ln\left\{\frac{a+1}{a-1}\right\},\ a \equiv \sqrt{2 + M/m} \quad (5)$$

Here M and m are the masses of the solute and solvent molecules, respectively. One is now in the position to estimate the rate of the angular momentum scrambling: $a = 2.89$, $\nu_J/z_c = 0.16$ for an I_2−Ar system and $a = 8.09$, $\nu_J/z_c = 0.02$ for an I_2−He system. The J-coherence counterparts of these quantities, calculated from the values of τ_c and τ_J given in Figure 3 of ref 1, are 0.18 and 0.023, respectively. In the limit $M/m \to 0$, eq 5 results in $\nu_J/z_c = 0.754$, while the J-coherence model yields[1] $\nu_J/z_c = 0.767$. So, eq 5 describes the ratio ν_J/z_c fairly well. On the other hand, $\nu_J = z_c(1-\gamma)$ in the KS model.[4−7] So, one can directly compare the predictions of the KS and J-coherence models by using the appropriate values of γ (see Figure 1). It turns out that the two models give rise to nearly

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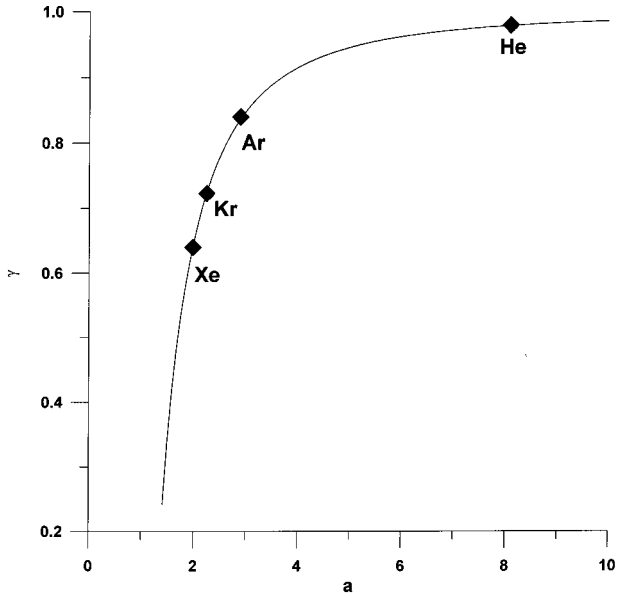

Figure 1. γ vs a − calculations on the basis of eq 5.

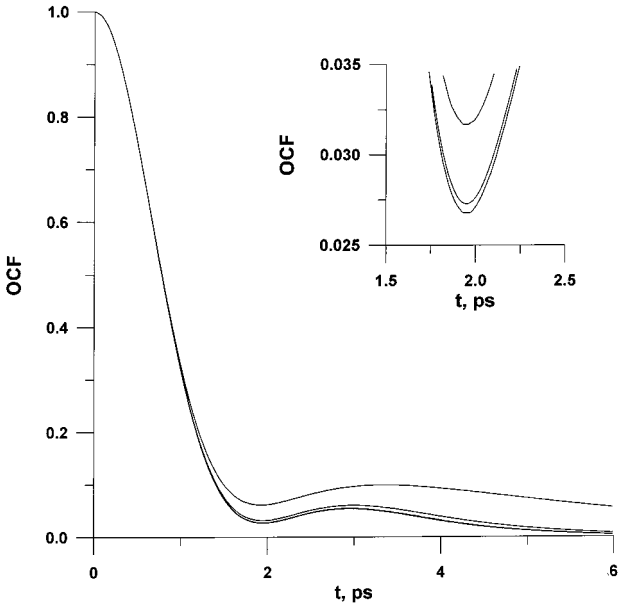

Figure 2. Time development of OCFs in the KS model for $\tau_J = 3$ ps. From top to bottom, the curves correspond to $\gamma = 0$ (the J-diffusion model), $\gamma = 0.84$ (I_2−Ar), $\gamma = 0.98$ (I_2−He), and $\gamma = 1$ (the FPE). The insert reproduces an amplified part of this same figure.

identicalbehavior for $r(t)$, both for I_2−Ar and for I_2−He systems. If plotted together, the J-coherence and the KS OCFs merge. So the KS model, equipped with formulas such as eq 5 or with more accurate Enskog-type expressions,[8] can successfully be used for the interpretation of experimental results. Work is in progress to generalize the KS model, to take into account the change of the molecular geometry after the optical excitation.

The above analyses raise the following important question. Zewail and co-workers showed that the friction model or, equivalently, the first cumulant expression for the OCF, was inadequate in reproducing their anisotropies and angular momentum relaxation times. It must however be stressed that it is not the failure of the Langevin description itself. It is an indication of the inadequacy of the above approximations for the OCF beyond their field of validity, i.e., beyond the hindered rotation limit. A rigorous calculation of the OCF in the Langevin theory is equivalent to the solution of the corresponding rotational FPE. This is given by eqs 1, 2, and 3′. The calculations

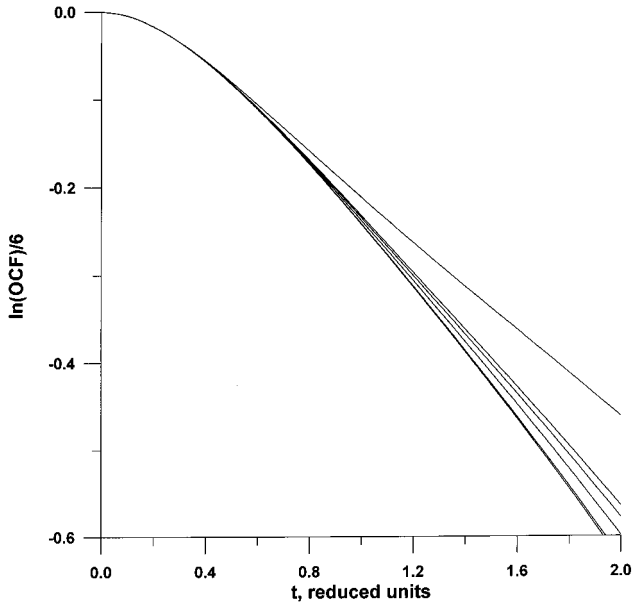

Figure 3. Logarithmic plots for the time development of OCFs in the KS model. $\nu_J = 3$. Time is given in units $(I/kT)^{1/2}$, and frequency in units $(kT/I)^{1/2}$, with I being the moment of inertia of a linear molecule. From top to bottom, the curves correspond to $\gamma = 0$ (the J-diffusion model), $\gamma = 0.64$ (I_2−Xe), $\gamma = 0.72$ (I_2−Kr), $\gamma = 0.84$ (I_2−Ar), $\gamma = 0.98$ (I_2−He), and $\gamma = 1$ (the FPE).

indicate that the OCFs predicted by the KS model, the FPE, and appear to be also OCFs predicted by the J-coherence model, are almost indistinguishable, both for I_2−Ar and for I_2−He systems. Figure 2 gives an estimation of the scale of differences between the approaches. So, it is practically impossible to discriminate between the OCFs given by the J-coherence, the KS, and the FPE models for such weak collisions. It would be desirable to perform real time polarization experiments with heavier buffer gas species, like Kr and Xe, which would give more pronounced differences between the predictions of the J-coherence and the KS models on one hand and the FPE on the other hand, see Figures 1 and 3. It also seems desirable to present the anisotropy decays in terms of logarithmic plots which amplify the difference between the curves at a short enough time interval (Figure 3).

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