

Rotational Relaxation of Free and Solvated Rotors

A.J. Bain, C. Han, P.L. Holt, P.J. McCarthy, A.B. Myers, M.A. Pereira, and R.M. Hochstrasser

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

1. Introduction

In most experimental studies of molecular motion in liquids the signals are averaged over many collisional periods and the processes observed are diffusive. When studies are carried out with sufficiently short light pulses it should become possible to observe nondiffusive behavior. In the case of molecular reorientation dynamics the nondiffusive portion corresponds to nearly free rotation. It is of great interest to study these transient regimes because of the detailed information that can be obtained about collision dynamics in condensed phases. While these transients are well known through studies of Rayleigh scattering [1], infrared, and Raman lineshapes [2] and from time domain Kerr effect studies in neat liquids [3,4], we are not aware of studies of nondiffusive effects involving the electronically excited states of molecules in dilute solutions. In the present paper we discuss fluorescence and polarization spectroscopy as methods of approach and present preliminary results which bring us closer to realizing these goals.

For a short period after ultrashort pulse excitation a molecule in a solution can be considered to be freely rotating inasmuch as it will have definite values of the angular momentum, J , and its projections onto laboratory- and molecule-fixed axes. The collisions will cause the initial J and its projections to randomize [5]. The initial situation corresponds closely to that which would prevail in a gas at the same temperature. We therefore began our investigations with studies of gases to try to observe the free rotation transients. We expect that when free rotation is rapid compared with collisions the nondiffusive behavior should be dominant whereas in the other limit the diffusional regime should be reached before the molecule can rotate significantly and the nondiffusive effect will be vanishingly small.

2. Fluorescence and Polarization Methods

In a fluorescence experiment the sample is excited with a short pulse of linearly polarized light and the time evolution of the fluorescence anisotropy, $r(t) = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$, is measured. In time-resolved polarization spectroscopy the decay of the anisotropy induced by a polarized excitation pulse is measured by probing with a second pulse polarized at 45° to the first and detecting the intensity transmitted through crossed polarizers. In solution, if the reorientation can be described as rotational diffusion, $r(t)$ decays as a sum of exponentials and the polarization spectroscopy signal decays as $S(t) = \exp[-2t/\tau_{ex}] [r(t)]^2$ where τ_{ex} is the excited state lifetime [6]. In a fluorescence experiment with collision-free rigid rotors, the intensity of α -polarized emission following a z -polarized delta-function excitation pulse is given by [7]

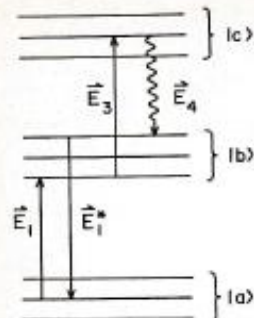


Fig. 1 Energy level diagram describing polarization spectroscopy and fluorescence anisotropy experiments. Levels b and b' may in general be the same or different states. In fluorescence, c is below b and b' in energy and the $b \rightarrow c$ and $b' \rightarrow c$ processes represent spontaneous emission.

$$I_{\alpha\alpha}(t) \propto \sum_{a,c} P_a \left| \sum_b e^{-i\omega_b t} C_a^{cb} C_z^{ba} \right|^2, \quad (1)$$

where a , b , and c are the initial, intermediate, and final rotational states (see Fig. 1), P_a is the initial population of state a , and $C_a^{cb} = \langle c | C_a | b \rangle$ is the direction cosine matrix element between the dipole axis of the molecule and space-fixed axis a . The vibrational states factor out of the anisotropy if vibration and rotation are separable. The polarization spectroscopy signal is given by

$$S(T) \propto \int_0^T dt [\hat{P}^{(3)}(t) \cdot \hat{E}_4]^2, \quad (2)$$

where T is the delay time between pump and probe pulses, and the macroscopic polarization $\hat{P}^{(3)}(t)$ is given for free rigid rotors by [7]

$$\hat{P}^{(3)}(t) \cdot \hat{E}_4 \propto i e^{i\omega_{cb} t} \sum_{a,c} P_a \left\{ \sum_b |C_1^{ba}|^2 C_3^{bc} C_4^{cb} e^{(i\omega_{cb} - \Gamma_{cb})(t-T) - \gamma_b T} + \sum_{b \neq b'} \sum_b C_1^{ba} C_1^{ab'} C_3^{b'c} C_4^{cb} e^{(i\omega_{cb} - \Gamma_{cb})(t-T) - (i\omega_{bb'} + \Gamma_{bb'})T} \right\}. \quad (3)$$

The pump, probe, and detected fields have polarizations \hat{E}_1 , \hat{E}_3 , and \hat{E}_4 . Γ_{cb} is the total dephasing constant between the final pair of levels, γ_b and $\Gamma_{bb'}$ are the population decay and dephasing constants for the intermediate state, and ω_{cb} is the vibronic transition frequency.

For collision-free molecules $r(t)$ does not in general decay to zero because the total angular momentum is conserved. For an ensemble of regular rotors at high J , there is a transient near time zero which decays to a constant value on a time scale of $\sim (I/KT)^{1/2}$ where I is the moment of inertia. This transient, which represents rigid-body rotational motion in a classical picture, arises in a quantum mechanical treatment from interferences between different intermediate rotational states that are coupled to the same pair of initial and final states [7] (Fig. 1). The anisotropy from a regular rotor in a particular initial J state would exhibit periodic recurrences, but the beating between different initial J 's cancels all but one of these recurrences, leaving a constant long-time anisotropy for the isolated molecule that depends on the inertial ratios [8,9]. Collisions will cause the long-time anisotropy to approach zero, but even at high collision rates

(i.e., in solution) the decay at very short times should resemble that for the free rotor.

The polarization spectroscopy signal for free rotors depends not only on the inertial ratios but also on the dephasing rate between the final pairs of coupled levels because this damps the macroscopic polarization in the medium. If dephasing is much faster than rotational periods, the polarization and fluorescence anisotropy decays are related by $S(t) = \exp[-2t/\tau_{\text{ex}}] [r(t)]^2$ as for rotational diffusion. If dephasing is slow compared with rotation, a different polarization decay is expected which bears no simple relationship to the fluorescence anisotropy (see Fig. 2). In addition there are phase matching constraints to consider. In two-beam polarization spectroscopy, contributions from diagonal terms in the second-order density matrix ($b' = b$ in Fig. 1) are exactly phase matched for all generated frequencies, while off-diagonal contributions (rotational CSRS processes) are not. The relative contributions to the signal from diagonal (non-oscillatory) and off-diagonal (oscillatory) terms thus depend on the spectral widths of the pulses relative to the spacing between P, Q, and R branches, the interaction length, and the angle between pump and probe beams [7]. Finally, even in the absence of vibration-rotation interaction, excitation of more than one intermediate vibrational state causes the nonlinear signal to decay at a rate determined by the energy spread of the coupled vibrational levels.

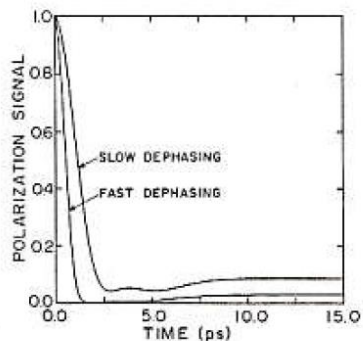


Fig. 2 Calculated polarization spectroscopy decays for fluorene modeled as a symmetric top in the fast and slow dephasing limits (see text). Rotational constants were $A=0.074 \text{ cm}^{-1}$ and $B=0.0175 \text{ cm}^{-1}$, at $T=443 \text{ K}$. Delta-function pulses were assumed. Signal strengths are not to scale; the signal is much stronger in the slow dephasing limit.

3. Results and Discussion

We have recently observed a free rotation transient in the fluorescence anisotropy of stilbene vapor (Fig. 3) [10]. An overall time resolution of 4-5 ps was achieved by upconverting the uv fluorescence in potassium pentaborate (KB5). The 302 nm excitation pulse was obtained by amplifying and doubling the output of a hybrid mode-locked dye laser, while the remaining undoubled light at 604 nm was used to gate the fluorescence. I_{\parallel} and I_{\perp} were obtained on successive scans by rotating the polarization of the excitation pulse between horizontal and vertical while upconverting only vertically polarized fluorescence. Both the observed zero-time anisotropy of 0.16 and the general shape of the anisotropy decay are reproduced quite well by convoluting the theoretical regular rotor decay with a 5 ps instrument function. The observed long-time anisotropy of 0.069 to 0.003 lies between the value of 0.074 expected for a regular rotor with stilbene's inertial ratios [9] and the value of 0.056 expected for fully statistical rotation in which extensive vibration-rotation coupling generates a microcanonical distribution of K levels for

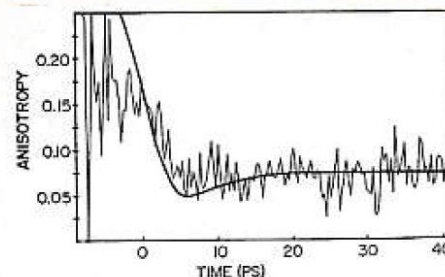


Fig. 3 Fluorescence anisotropy decay of trans-stilbene vapor at 463 K, ~ 1 torr, with 302 nm excitation. The smooth curve is the theoretical decay for a symmetric top with $A=0.0908 \text{ cm}^{-1}$ and $B=0.00865 \text{ cm}^{-1}$. A Gaussian instrument function of 5 ps FWHM was used.

each J state [8]. This indicates that the hot (463 K) stilbene molecule excited 650 cm^{-1} above the origin undergoes partial but incomplete vibration-rotation energy transfer within approximately one rotational period. Lower long-time anisotropies were previously observed at higher excess energies [11]; the limiting anisotropy of 0.05 observed with excitation 5000 cm^{-1} above the origin corresponds to essentially statistical rotation.

Figure 4 shows the polarization spectroscopy response of fluorene vapor. Excitation and probe pulses (296 nm, 4 ps and 592 nm, 6 ps) were derived from an excimer amplified synchronously pumped dye laser system [12]. The constant signal level observed from a few ps to 250 ps indicates the absence of any vibration-rotation coupling that could destroy the anisotropy on this time scale. Fluorescence experiments [13] yielded a value of 0.066 for the anisotropy of fluorene excited at its 0-0 transition, indicating that it behaves as a regular rotor. We have determined that the small spike at zero time in the polarization experiment originates from the cell windows. No free rotation transient due to the vapor can be discerned. However, this is consistent with calculations in which the appropriate pulse widths and phase matching conditions are included. This indicates the need for pulse widths that are closer to the 1.7 ps free rotation time of fluorene.

In addition to the vapor phase work, we have obtained fluorescence anisotropy decays for stilbene in low and high viscosity solvents [10]. The decays are fit well to single exponential rotational diffusion times of 11 and 78 ps

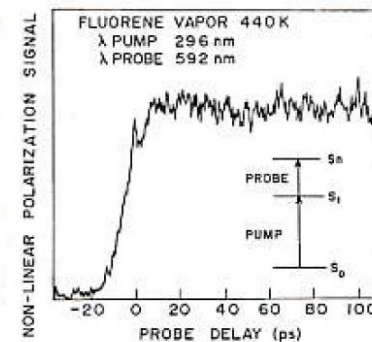


Fig. 4 The time-resolved polarization spectroscopy signal from collision-free fluorene. The spike at zero probe delay originates from window adsorbed species.

in isopentane and hexadecane, respectively, with corresponding zero-time anisotropies of 0.39 and 0.36. No nondiffusive behavior, which would be manifested as a rapid decrease in the anisotropy near $t=0$, is apparent.

Motions such as the in-plane spinning of benzene and substituted benzenes require little solvent displacement and appear more likely to exhibit reorientation by free rotation. Previous investigations using NMR and light scattering concluded that the rotational relaxation times for spinning are much shorter than predicted by standard hydrodynamic theory and are nearly independent of viscosity [1]. We have recently obtained fluorescence anisotropy decays for a substituted benzene, aniline, to directly measure these orientational correlation functions (Fig. 5). Fitting the data to single exponential decays yields rotational relaxation times that differ by only a factor of two between isopentane ($\eta=0.22$ cp) and hexadecane ($\eta=3.3$). The electronic transition is b-axis polarized (in the plane of the ring perpendicular to the CN bond) so the fluorescence can depolarize by rotation about both the a and c axes. "Slip" boundary conditions [14] predict rotational diffusion times of $\tau_a=0.7$ ps, $\tau_c=0.1$ ps in isopentane and $\tau_a=10$ ps, $\tau_c=1.6$ ps in hexadecane. The τ_c values are small because aniline is a near-oblate ellipsoid and rotation about the symmetry axis of a symmetric top experiences no friction in the slip limit. Presumably the above rotational diffusion times should be added to the free rotation times (the expected zero-viscosity intercepts) of $\tau_a=0.4$ ps, $\tau_c=0.7$ ps. It is difficult to determine how well our data follow slip hydrodynamics because we cannot reliably fit multiple exponentials to the anisotropy decays and because τ_a , in particular, is sensitive to the axial ratios used [14]. However, even in hexadecane the overall reorientation time is within a factor of five of the free rotation time.

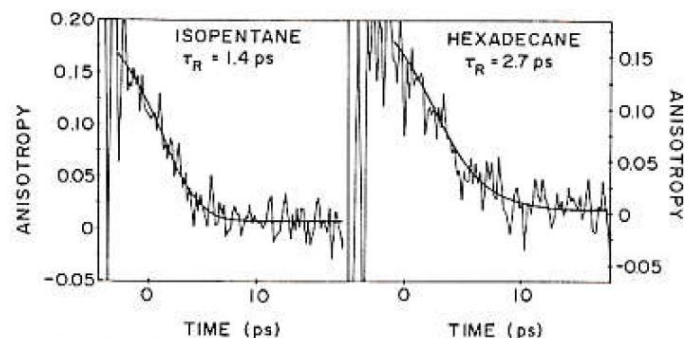


Fig. 5 Fluorescence anisotropy decays of aniline with 302 nm excitation. The smooth curves are the best fits to single exponential decays.

4. Conclusions

We have observed a transient in the fluorescence anisotropy of stilbene vapor that can clearly be attributed to free inertial rotation. In contrast, polarization spectroscopy did not resolve any such transient in fluorene vapor. As discussed above, several factors other than purely rotational dynamics contribute to the four-wave mixing decays and could render the free rotation transient less apparent. While these factors complicate the analysis of four-wave mixing data, they can also provide additional information. For

example, by changing the interaction length or the angle between pump and probe beams it may be possible to experimentally separate the diagonal and off-diagonal contributions to the polarization signal. Comparison of polarization spectroscopy and fluorescence anisotropy decays may also allow determination of the dephasing constant Γ_{bc} in (3). It should now be feasible to apply fluorescence methods to examine the extent of free rotation of medium-sized molecules in liquids, dense gases, and supercritical fluids. Preliminary results suggest that free rotation may contribute considerably to reorientation of aniline in solution. Such studies will provide an important link between previous work on rotational diffusion in larger molecules performed with lower time resolution and lineshape studies carried out on smaller molecules.

5. Acknowledgments

This work was supported by grants from NSF and NIH. A.B.M. is an NIH post-doctoral fellow.

6. References

1. B. J. Berne and R. Pecora: Dynamic Light Scattering (Wiley, New York 1976), chapter 7
2. J. H. R. Clarke: In Advances in Infrared and Raman Spectroscopy, ed. by R. J. H. Clark and R. E. Hester, vol. 4 (Heyden, London 1978)
3. J. M. Halbout and C. L. Tang: Appl. Phys. Lett. **40**, 765 (1982)
4. B. I. Greene and R. C. Farrow: In Picosecond Phenomena III, ed. by K. B. Eisenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau (Springer-Verlag, Berlin, Heidelberg 1982)
5. R. G. Gordon: J. Chem. Phys. **44**, 1830 (1966)
6. A. B. Myers and R. M. Hochstrasser: IEEE J. Quantum Electron., in press
7. A. B. Myers and R. M. Hochstrasser: J. Chem. Phys., submitted
8. G. M. Nathanson and G. M. McClelland: J. Chem. Phys. **81**, 629 (1984)
9. A. P. Blokhin and V. A. Tolkahev: Opt. Spectrosc. **51**, 152 (1981)
10. A. B. Myers, P. L. Holt, M. A. Pereira, and R. M. Hochstrasser: Chem. Phys. Lett., submitted
11. D. K. Negus, D. S. Green, and R. M. Hochstrasser: Chem. Phys. Lett. **117**, 409 (1985)
12. A. J. Bain, P. J. McCarthy, and R. M. Hochstrasser: Chem. Phys. Lett. **125**, 307 (1986)
13. A. B. Myers and R. M. Hochstrasser: Unpublished results
14. G. K. Youngren and A. Acrivos: J. Chem. Phys. **63**, 3846 (1975)