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Abstract. The Raman spectra of reacting molecules in liquids can yield information about various aspects of the reaction dynamics. We discuss the analysis of Raman spectra for three prototypical unimolecular reactions, the rotational isomerization of n-butane and 1,2-difluoroethane, and the barrierless exchange of axial and equatorial hydrogens in cyclopentane via pseudorotation. In the first two cases the spectra are sensitive to torsional oscillations of the gauche conformer, and yield estimates of the torsional solvent friction. In the case of cyclopentane, the spectra can be used to discriminate between different stochastic models of the pseudorotation dynamics, and to determine the relevant friction coefficients.

1. Introduction

Conventional, frequency-domain Raman spectroscopy can provide a useful probe of reaction dynamics in solution. While motion along the reaction coordinate may not be directly observable in the spectrum, the reaction dynamics may still be reflected in the bandshapes of other Raman active modes that couple to the reaction coordinate [1, 2]. By analyzing these Raman bandshapes one can study quite rapid motions along the reaction coordinate, since the characteristic vibrational timescale set by the linewidths in the spectrum is usually of the order of picoseconds or less.

We have recently used this approach to study conformational dynamics in liquid n-butane [3] and liquid cyclopentane [4]. Both of these systems can be viewed as simple prototypes for unimolecular reactions with quasi one-dimensional reaction coordinates. In n-butane the reaction involves the rotational isomerization between gauche and trans conformers, and the barrier is sufficiently high that reactive, interwell dynamics should have no observable affect on the Raman spectrum. However, certain Raman bands of the gauche conformer are broadened by intrawell torsional dynamics, and an analysis of this broadening leads to experimental estimates for the solvent friction on the reaction coordinate within his potential well [3]. In cyclopentane, the 'reaction' involves the barrierless exchange of axial and equatorial hydrogens via pseudorotation, and the CH stretching spectrum of cyclopentane-d_9 provides a sensitive indicator of the influence of the solvent on the pseudorotation dynamics [4].

Here we summarize recent extensions of this work, including an examination of the solvent dependence of the torsional friction in n-butane [5], a study of torsional friction

in liquid 1,2-difluoroethane [6], and a more detailed analysis of the Raman spectrum and pseudorotation dynamics of cyclopentane-d_9 [7].

2. Torsional dynamics of n-butane

In the case of n-butane, we have shown previously that the Raman active in-phase CCC bending mode couples strongly to the torsional coordinate through the kinetic energy, and thus provides a useful probe of the torsional dynamics [3]. The bending frequency is relatively insensitive to changes in the torsion angle near the trans minimum in the torsional potential, but near the gauche minimum the bending frequency shifts linearly with changes in the torsion angle. The resulting dephasing and broadening of the gauche band due to torsional fluctuations is given by

$$\Gamma_g = (2\pi c \, \partial \nu / \partial \varphi)^2 \langle (\delta \varphi)^2 \rangle \tau \qquad (1)$$

where c is the speed of light, $\partial \nu / \partial \varphi$ is the change in the gauche bending frequency with torsion angle φ, and $\langle (\delta \varphi)^2 \rangle$ and τ are the mean square amplitude and correlation time of torsional fluctuations in the gauche well, respectively. If the torsional fluctuations are modelled using the generalized Langevin equation for a damped, harmonic oscillator [8], then the torsional correlation time will be given by

$$\tau = \beta(0)/\Omega^2 \qquad (2)$$

where $\beta(0)$ is the zero-frequency torsional damping coefficient, which is proportional to the zero-frequency solvent friction, and Ω is the torsional frequency. Thus, a measurement of Γ_g will yield values for τ or $\beta(0)$, since all of the other parameters in equations (1) and (2) are known or readily estimated [3]. We have determined Γ_g from the difference in the isotropic Raman linewidths of the gauche and trans bending bands, since only the gauche band should show appreciable broadening by torsional fluctuations. This assumes that other contributions to the linewidths of the two bands will cancel. (Alternatively, one can obtain upper bounds for τ and $\beta(0)$ from the full gauche linewidth.)

We have extended our earlier results for neat n-butane [3] by determining the torsional correlation times τ for gauche n-butane in four different solvents, carbon disulphide, benzene, cyclopentene, and methanol [5]. The resulting τ values are similar in magnitude to those found for neat liquid n-butane, and also show a similarly weak temperature dependence. In figure 1 we show a plot of τ versus solution viscosity for the carbon disulphide, cyclopentene, and methanol solutions, which span the range of behaviour seen in all of the solvents. If the friction relevant to these torsional oscillations were hydrodynamic, one would expect the plots to be linear; it is clear from figure 1 that the torsional friction is decidedly non-hydrodynamic. The non-linearity in these plots is quite similar to what has sometimes been observed for the barrier friction in photo-isomerization reactions [9, 10], and the same empirical power law function often used to fit the barrier friction data provides a reasonable description of our data, as indicated by the solid lines in figure 1. In the case of barrier friction this power law behaviour has sometimes been attributed to the fact that the barrier may emphasize the high-frequency friction [11, 12], but in our case it is the low-frequency friction that is measured.

We also find that an Enskog model for friction [3] gives rise to values of τ that are in good agreement with the data for all of the solvents, both in magnitude and in temperature dependence. The use of recently published effective hard sphere diameters
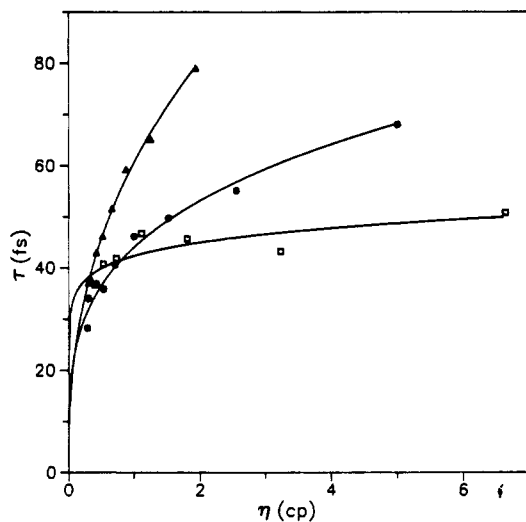
Figure 1. Torsional correlation times τ versus solution viscosity η for n-butane in three different solvents, carbon disulphide (triangles), cyclopentene (filled circles), and methanol (open squares). The concentrations of n-butane in these solutions were 16, 25, and 19 mol%, respectively. The solid lines are fits of these data sets to a power law of the form $\tau = b\eta^a$, with the values of the exponent being 0.41, 0.27, and 0.09, respectively.
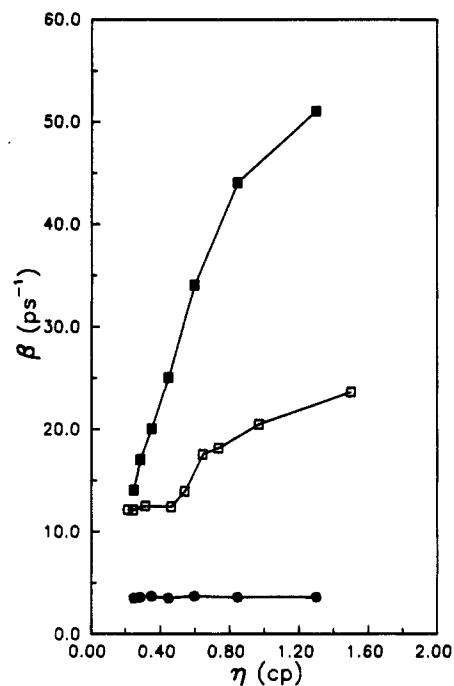
Figure 2. The viscosity dependence of the zero-frequency friction coefficients $\beta(0)$ for torsional oscillations of the gauche conformer in neat liquid 1,2-difluoroethane (filled squares) and neat liquid n-butane (open squares), and the high-frequency friction coefficient $\beta(\Omega)$ for torsional oscillations of gauche 1,2-difluoroethane in the neat liquid (filled circles).

[13] for the solvents in this calculation yields a significant improvement over our earlier calculations [3]. Since the Enskog model incorporates only uncorrelated binary collisions and not the correlated, collective motions that dominate the macroscopic viscosity, the success of this model may indicate that the torsional friction is dominated by local, short-range interactions. This could occur because the small amplitude of the torsional fluctuations emphasizes the short-distance, or high-wavevector solvent friction. Oxtoby has put forth a similar argument to explain the success of the binary collision model in studies of vibrational dephasing in liquids [14].

3. Torsional dynamics of 1,2-difluoroethane

We have also used this same methodology to determine zero-frequency torsional friction coefficients $\beta(0)$ in liquid 1,2-difluoroethane [6]. This molecule is nearly identical to n-butane in terms of the kinematics of the CCF bending and torsional vibrations, but the torsional potential is somewhat different [15] and there is a large stabilization of the dipolar gauche form in solution [16]. The presence of this strong dielectric interaction

with the solvent could lead to a significant contribution to the torsional friction from dielectric friction [17]. In addition, in 1,2-difluoroethane the torsion band of the gauche conformer is directly observable in the Raman spectrum near $170\,\text{cm}^{-1}$. The width of this band contains contributions from both pure dephasing and population relaxation processes, the latter being given by $\beta(\Omega)/2$, where $\beta(\Omega)$ is the friction coefficient evaluated at the torsional frequency. We can calculate the dephasing contribution [8] using the $\beta(0)$ values determined from the bending linewidths and the cubic anharmonicity of the torsional potential, and we find this contribution to be considerably smaller than the observed linewidth of the torsion band. Thus, for this molecule we can determine both the low-frequency friction $\beta(0)$ *and* the high-frequency friction $\beta(\Omega)$ from the bending and torsion linewidths, respectively.

In figure 2 we show a plot of both $\beta(0)$ and $\beta(\Omega)$ versus viscosity for neat liquid 1,2-difluoroethane, and we also include the $\beta(0)$ data for neat liquid n-butane [3] for comparison. The fact that the magnitudes of the $\beta(0)$ values and their viscosity dependences are so similar for 1,2-difluoroethane and n-butane suggests that dielectric friction does not make a major contribution to $\beta(0)$. This is reasonable since dielectric friction results from the time lag in the response of the solvent to a change in the solute dipole, and at zero frequency the solvent can follow the solute adiabatically. Figure 2 also shows that the high-frequency friction coefficient $\beta(\Omega)$ is much smaller in magnitude than $\beta(0)$, and essentially independent of temperature and viscosity. This behaviour can be rationalized on the basis of the relatively high torsional frequency of $\Omega \approx 30\,\text{ps}^{-1}$. This frequency is considerably higher than the longitudinal relaxation frequency τ_L^{-1} [17] that characterizes the dielectric friction in 1,2-difluoroethane, so that on the timescale of Ω^{-1} the solvent dipoles will not be able to respond and will only contribute a 'frozen' dipolar potential, rather than dielectric friction. In addition the frequency Ω is also much higher than the characteristic frequencies associated with the collective motions that characterize the viscosity, so that $\beta(\Omega)$ should bear little relation to the macroscopic solvent friction. In keeping with the hypothesis presented for the n-butane solution data, $\beta(0)$ may represent the high-wavevector, zero-frequency solvent friction, whereas $\beta(\Omega)$ may represent the solvent friction evaluated at both high-wavevector and high-frequency.

4. Pseudorotation dynamics in liquid cyclopentane

In a previous publication [4] we showed that the CH stretching bands in the isotropic Raman spectrum of liquid cyclopentane-d_9 are partially motionally averaged by pseudorotation, a barrierless conformational rearrangement that rapidly changes the character of CH bonds between axial and equatorial. The coupling potential between the CH stretching vibration and the pseudorotation angle was determined using *ab initio* CH bond lengths in conjunction with an empirical correlation between deuterium-isolated CH stretching frequencies and CH bond lengths. This coupling potential was then incorporated in a stochastic Liouville equation [18] to model the experimental lineshapes. A diffusive model for pseudorotation that included exponentially decaying temporal memory provided a good fit to the spectra, and yielded an effective pseudorotation angular momentum relaxation frequency that was independent of temperature. However, the value of this relaxation frequency was only twice the inertial frequency for pseudorotation, indicating the inadequacy of the diffusive model.
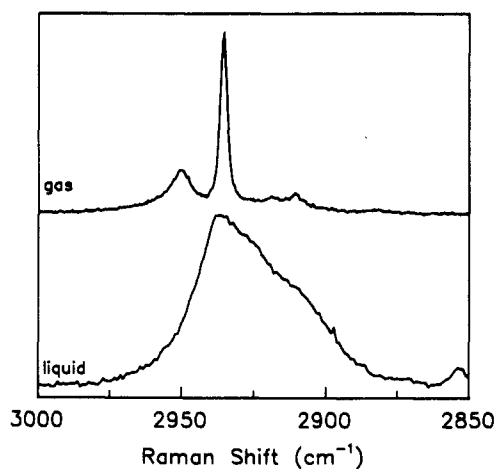
Figure 3. Isotropic Raman spectra of cyclopentane-d_9 in the CH stretching region for the gas and liquid phases at room temperature. The intensity scales of the two spectra are not the same.

Since that publication we have obtained the gas phase Raman spectrum of cyclopentane-d_9, we have examined the spectrum in several different solvents, and we have explored other dynamical models for pseudorotation that explicitly incorporate inertial motion [7]. Figure 3 compares the gas phase CH stretching spectrum of cyclopentane-d_9 with that of the liquid. The structure in this spectrum results almost entirely from the coupling to pseudorotation, and the dramatic change in shape on going to the liquid reflects the change in the pseudorotation dynamics brought about by solvent collisions. A gas phase spectrum calculated using an adiabatic approximation with the previous coupling potential [4] and 'free' pseudorotation is in good agreement with the experimental spectrum, indicating that we have a good model for the potential. This potential has been used with both BGK [19] and Fokker–Planck [20] models for the pseudorotation dynamics to calculate spectra as a function of collision rate of friction. Both models give gas phase spectra that match experiment, but only the Fokker–Planck model provides an adequate fit to the experimental spectrum of the liquid. The 'true' collision rate that results from these fits is essentially equal to the inertial frequency, and shows little variation with temperature in the liquid, in agreement with the results obtained with the diffusive model [4]. Similar behaviour is observed for the friction in several other solvents, including methylene chloride-d_2, carbon tetrachloride, methanol-d_4, and carbon disulfide. Once again this behaviour can be rationalized if the wavevector dependence and/or frequency dependence of the solvent friction is important.

Acknowledgments

References

[1] MacPhail R A and Strauss H L 1985 *J. Chem. Phys.* **82** 1156

[2] Viot P, Tarjus G, Borgis D and Bratos S 1989 *J. Chem. Phys.* **90** 7022
[3] MacPhail R A and Snyder R G 1989 *J. Chem. Phys.* **91** 3895
[4] MacPhail R A and Variyar J E 1989 *Chem. Phys. Lett.* **161** 239
[5] Cates D A and MacPhail R A submitted
[6] MacPhail R A and Monroe F C 1990 *Chem. Phys.* at press
[7] Variyar J E 1990 *PhD Dissertation* Duke University
[8] Levine A M, Shapiro M and Pollak E 1988 *J. Chem. Phys.* **88** 1959
[9] Courtney S H and Fleming G R 1985 *J. Chem. Phys.* **83** 215
[10] Lee J, Zhu S-B and Robinson G W 1987 *J. Phys. Chem.* **91** 4273
[11] Grote R F, van der Zwan G and Hynes J T 1984 *J. Phys. Chem.* **88** 4676
[12] Bagchi B and Oxtoby D 1983 *J. Chem. Phys.* **78** 2735
[13] Ben-Amotz D and Herschbach D R 1990 *J. Phys. Chem.* **94** 1038
[14] Oxtoby D W 1979 *J. Chem. Phys.* **70** 2605
[15] Takeo H, Matsumura C and Morino Y 1986 *J. Chem. Phys.* **84** 4205
[16] Abraham R J and Kemp R H 1971 *J. Chem. Soc.* B 1240
[17] van der Zwan G and Hynes J T 1985 *J. Chem. Phys.* **88** 4181
[18] Kubo R 1969 *Adv. Chem. Phys.* **15** 101
[19] Montgomery J A Jr, Chandler D and Berne B J 1979 *J. Chem. Phys.* **70** 4056
[20] Evans G T 1983 *J. Chem. Phys.* **78** 4963