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Forced Rayleigh scattering studies of mixtures of amplitude and phase gratings in methyl yellow/alcohol solutions

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Forced Rayleigh scattering (FRS) studies have been carried out on methyl yellow/alcohol solutions at two different probe wavelengths (633 and 543 nm). The signal shapes observed at the two wavelengths are quite different: using ethanol and 2-propanol as solvents, we observe at 633 nm a decay–grow–decay (DGD) shape similar to profiles frequently reported in the literature, while at 543 nm we observe a DGD shape in which the signal at the local minimum does not reach the baseline. In principle, the nonzero minimum can be accounted for by a difference (due to amplitude/phase-grating mixtures) in the phase shifts of light scattered from the photoproduct and ground-state molecules. To test this hypothesis, we first show in a straightforward manner that the signal can be approximated as the product of a polynomial and an exponential decay, which allows for data reduction of profiles with zero or nonzero phase-shift differences. Using this approach, the diffusion coefficients measured using the two probe wavelengths are found to be the same to within an uncertainty of 2%–3%. The results provide strong evidence that the difference in signal shapes is caused by amplitude/phase-grating mixtures within the methyl yellow/alcohol system, and imply that diffusion coefficients can be measured without difficulty for other FRS systems characterized by such mixtures. © 2000 American Institute of Physics. [S0021-9606(00)01621-4]

INTRODUCTION

Forced Rayleigh scattering (FRS) has become a powerful tool for studies of mass diffusion within fluid media on length scales of 1–100 μm.1–22 In the FRS method, interference fringes created by coherent crossed “pump” laser beams are used to excite dye molecules within the medium of interest, creating a spatially periodic modulation in the photoproduct population distribution. Since each photoproduct is formed at the expense of a ground-state dye molecule, the photoproduct population distribution. Since each photoproduct and ground-state molecules diffuse (in general) at different rates, there are, in fact, “complementary” photoproduct and ground-state gratings that form within the sample and subsequently decay.23–26

The two gratings are commensurate, with the minima in the photoproduct grating coincident with the maxima in the ground-state grating. A Bragg-incident probe beam diffracted from the gratings is used to monitor the decay of the periodic concentration profile as the dye molecules diffuse after the crossed pump beams are switched off. The rate at which the diffracted signal decays provides direct information on the diffusion of the dye molecules on the length scale set by the interference fringe spacing.

Each of the two gratings in a FRS experiment can be either a “phase grating” or an “amplitude grating” (corresponding to a spatial modulation in the real or imaginary part, respectively, of the refractive index difference between the dye and the solvent), or a phase-amplitude mixture.23,27,28 A system in which both the photoproduct and ground states form pure-amplitude gratings is possible in principle but unlikely in practice, since (as shown by Fayer and co-workers28,29) phase contributions will always be significant unless a grating is probed at a wavelength very close to an absorption maximum. In any case, pure phase gratings provide the largest diffraction efficiencies27 and are commonly used in FRS measurements. Discussions of the profile shapes for pure phase gratings have appeared frequently in the FRS literature: in this instance, the photoproduct and ground-state gratings will be 180° out of phase, and the FRS signal will involve a difference of two exponential decays.23–25 Thus, if the diffusion coefficients for the two gratings are D1 and D2 and the scattering amplitudes have magnitudes A1 and A2, then the detected homodyne signal follows the “standard” FRS model equation,

\[ V(t) = (A_1 \exp[-r_1 t] - A_2 \exp[-r_2 t])^2, \]  

where \( r_i = q^2 D_i \) , q is the grating wave vector, and we have assumed that appropriate experimental methods (as discussed by several authors \( ^1,16,23,30 \)) have been employed to eliminate the coherent baseline. The time \( t = 0 \) represents the instant at which the pump beams are switched off. To describe the profile shapes associated with Eq. (1), it is useful, as a mathematical convenience, to envision the time \( t \) extending over positive and negative values. There are then exactly two times at which the derivative \( dV/dt \) is equal to zero. When \( dV/dt \) vanishes at zero, one, or two positive
times, the profile shape is known as a decay-only (DO), grow–decay (GD), or decay–grow–decay (DGD) profile, respectively. A DGD-type profile described by Eq. (1), which displays both a local minimum and a local maximum for \( r>0 \), occurs if (and only if) one of the joint conditions \( \{A_2/A_1,1>1 \text{ and } r_2/r_1,>1 \} \) or \( \{A_2/A_1<1 \text{ and } r_2/r_1<1 \} \) is satisfied. The signal level at the local minimum of a DGD profile described by the “standard” model equation [Eq. (1)] will always be zero. It should also be noted that, according to Eq. (1), a distinct DGD shape is possible for an arbitrarily small nonzero difference between \( r_1 \) and \( r_2 \) if the difference between \( A_1 \) and \( A_2 \) is also small; hence, it is not surprising that DGD profiles appear frequently in the FRS literature.

In this work, we report on investigations of a dye/solvent system yielding FRS profiles that in some cases cannot be described by the “standard” FRS model equation [Eq. (1)]. The system, consisting of an azo dye (methyl yellow, MY) in alcohol, has been studied using two different probe wavelengths, 633 and 543 nm. Data acquired at 633 nm display a minimum that reaches the baseline and can be satisfactorily accounted for by Eq. (1); however, the signal observed at 543 nm has a nonzero minimum and cannot be described even approximately by Eq. (1). Since the photoproduct state of the dye absorbs weakly at 543 nm, we propose that the signal shape for this probe wavelength is due to the presence of both amplitude and phase contributions to the photoproduct grating, so that the photoproduct grating is a “mixed” grating. This hypothesis is then tested by measuring the mean photoproduct/ground-state diffusion coefficient independently at the two different probe wavelengths using a new approach to FRS data analysis.

The subject of amplitude/phase-grating mixtures in general and the extraction of useful information on mass diffusion from mixed gratings in particular are highly relevant topics for accurate FRS studies, insofar as such mixtures are expected to occur whenever the probe beam is partially absorbed by either the photoproduct or ground-state molecules. The importance of the subject notwithstanding, we are unaware of any previous experimental studies in which FRS time profiles were used explicitly for tests for amplitude/phase grating mixtures within a simple two-grating system. We note that the subject has been addressed theoretically and via simulations, and that measurements of the wavelength dependence of the relative amplitude- and phase-grating contributions to the diffraction efficiency have been reported by Nelson et al.

**RESULTS AND DISCUSSION**

The FRS decay profiles of MY in EtOH and 2-ProOH recorded at probe-beam wavelengths of 633 and 543 nm are shown in Fig. 1. The poorer signal-to-noise ratio obtained at 543 nm results mainly from the reduction in probe-beam transmission due to absorption by cis-MY at this wavelength. For the decay profiles recorded with a 633 nm probe-beam wavelength in both ethanol and 2-propanol, the local minimum reaches the baseline. The 633 nm profiles are thus examples of the “standard DGD” FRS curve for pure phase gratings. In Figs. 1(a) and 1(b), the upper profiles have been fit to Eq. (1) using standard nonlinear regression methods. It is interesting to note that single-exponential profiles (rather than DGD shapes) have been reported for a 633 nm probe wavelength in MY in hydrophobic solvents. Since the refractive index of the cis form of azobenzene derivatives is known to be smaller than that of the trans form, the DGD-
type profile indicates that the diffusion of cis-MY must be slower than trans-MY in alcohols. The slowing of the cis isomer is probably due to its higher dipole moment, which induces stronger solvation in polar solvents. Chan and co-workers have observed retarded diffusion of polar aromatic molecules due to solvation effects in Taylor dispersion experiments. Slowing due to solvation has also been discussed by Terazima et al. Although the fits to Eq. (1) of the 633-nm data in Figs. 1(a) and 1(b) appear quite satisfactory, it should be kept in mind that the individual $A_i$ and $r_i$ listed are not particularly meaningful, since it has been well established that fits to Eq. (1) are, in general, not unique. It is possible to alter the initial guesses and find a set of $A_i$ and $r_i$ different from those reported in Figs. 1(a) and 1(b) that fit the data equally well. It has been argued that the meaningful rate constant in a FRS decay described by Eq. (1), which can be measured in a unique manner, is the mean of the $r_i$. Simple data-analysis methods for obtaining a unique mean rate constant without resort to nonlinear regression have been discussed by Park et al., who pointed out that the average rate constant is approximately the reciprocal of the time difference between the local maximum and minimum, and Spiegel et al., who noted that the mean rate could be inferred from the curvature at the local maximum.

In contrast to the profiles obtained at 633 nm, the signals obtained with the 543 nm probe beam consistently display a local minimum lying well above the baseline: as shown in Figs. 1(c) and 1(d), the signal at the local minimum is about 85% (35%) of the signal at the local maximum in EtOH (2-ProOH) for a 543 nm probe wavelength. Because of the observed nonzero minimum, the “standard” FRS model equation [Eq. (1)] clearly cannot describe the 543 nm data. On the other hand, a nonzero minimum is expected if either the photoproduction or the ground-state grating is a mixed amplitude/phase grating, since in this case the phase difference between the two gratings is no longer 180°. The effect of probe-beam absorption on the phase of the diffracted light is easily understood: if the probe beam is absorbed (for example) by photoproduction molecules, then the field diffracted from the photoproduction grating will be shifted in phase by the angle

$$\phi_p = \tan^{-1}\left(\frac{-\Delta n_p}{\Delta k_p}\right),$$

where $\Delta n_p$ and $\Delta k_p$ are the real and imaginary parts, respectively, of the refractive index difference between the photoproduction and the solvent. Similarly, if the probe beam is absorbed by ground-state molecules, the field diffracted from the ground-state grating is shifted in phase by the angle

$$\phi_g = \tan^{-1}\left(\frac{-\Delta n_g}{\Delta k_g}\right),$$

where $\Delta n_g$ and $\Delta k_g$ are the real and imaginary parts of the refractive index difference between the ground-state dye molecules and the solvent. As a result of the phase shifts $\phi_p$ and $\phi_g$, the homodyne FRS signal obtained from mixtures of phase and amplitude gratings takes the form

$$V(t) = |A_1 \exp[-r_1 t] - e^{i \Delta \phi} A_2 \exp[-r_2 t]|^2,$$

where $\Delta \phi = \phi_p - \phi_g$. The local minimum in Eq. (4) is nonzero whenever $\Delta \phi \neq 0$. The solid-line curves in Fig. 2 show examples of profiles generated using Eq. (4) for various $\Delta \phi$ with the $A_i$ and $r_i$ held fixed.

Since the photoproduct state of MY absorbs weakly at 543 nm, but displays negligible absorption at 633 nm, while the ground-state absorption is nearly zero at both wavelengths, a simple explanation for the profile-shape difference for the 633 and 543 nm probes is that the photoproduct MY grating is a mixture of amplitude and phase contributions. Equation (4) should then describe both the 633 and 543 nm data, with $\Delta \phi = 0$ at 633 nm and $\Delta \phi \neq 0$ at 543 nm. As a direct test of the mixed-grating hypothesis, one could measure the mean of the photoproduct and ground-state grating decay rates independently at each probe wavelength, using Eq. (4) to model the data. The only difference in the investigations at 633 and 543 nm is the wavelength at which the gratings are probed. If indeed the sole reason for the shape difference is the presence of a mixture of amplitude and phase gratings at 543 nm, then the grating dynamics should be identical at the two different probe wavelengths. Thus, if the measured mean rate constants are not the same at 633 and 543 nm, then the amplitude/phase-mixtures hypothesis cannot be a complete explanation for the observed MY/alcohol FRS signals.

In testing this hypothesis, the manner in which the 543 nm data should be reduced is not immediately obvious. Nonlinear regression methods introduce significant complications since this approach does not provide (in general) unique fits, even in the case $\Delta \phi = 0$. Simplified methods published previously for obtaining average rate constants from non-exponential FRS curves assume a minimum of zero and hence are not appropriate for the 543 nm data. Thus, there is a need for a new, simple, and more general approach to the reduction of FRS data appropriate for both the cases $\Delta \phi = 0$.

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**FIG. 2.** The solid lines represent simulated FRS curves obtained from Eq. (4). For all profiles, the amplitudes are $A_1 = 1.00$ and $A_2 = 1.10$, and the rate constants are $r_1 = 1.00$ and $r_2 = 1.30$. The different values employed for the phase difference $\Delta \phi$ are listed on the right-hand side. Each profile has been normalized to its value at $t = 0$, and offsets have been added for clarity. The simulated data represented by the individual points are derived from the approximation indicated in Eq. (6), with values for the polynomial coefficients $a$, $b$, and $c$ calculated as discussed in the text. The good agreement between the solid lines and the individual points demonstrates the validity of the approximation.
and $\Delta \phi \neq 0$. Here we propose such a method. We note first that Eq. (4) can be rearranged to the equivalent form

$$V(t) = 4A_1 A_2 \exp[-2 r_{av}^2] \sinh[(\Delta r/2)(t-t_0)^2],$$

(5)

where $r_{av} = (\bar{r}_2 + \bar{r}_1) / 2$, $\Delta r = r_2 - r_1$, and $t_0 = (\Delta r)^{-1} \times (\ln[A_2/A_1] + i \Delta \phi)$. For many FRS dye molecules (including the azobenzenes)\textsuperscript{24,26} the ratios $r_2/r_1$ and $A_2/A_1$ will not differ greatly from unity. In addition, in most experiments the phase difference $\Delta \phi$ will be small compared to 1 rad (expected whenever the $\Delta k_i$ are small, or when the photoproduct/ground-state absorption coefficients are not very different)\textsuperscript{28} When these conditions are satisfied, Eq. (5) can be expanded about the time $t_0$ to yield a very simple form for $V(t)$:

$$V(t) = (at^2 + bt + c) \exp(-2 r_{av} t),$$

(6)

where $a = A_1 A_2 \Delta r^2$, $b = -2 A_1 A_2 (\Delta r) \ln(A_2/A_1)$, and $c = A_1 A_2 [(\ln(A_2/A_1))^2 + (\Delta \phi)^2]$. Equation (6) contains four unknown parameters [one less than Eq. (4)]. For the special case $\Delta \phi = 0$, the polynomial preexponential term in Eq. (6) reduces to the form $(\text{const}) \times (t-t_0)^2$. To demonstrate the validity of the approximation, curves with $r_2/r_1 = 1.30$ and $A_2/A_1 = 1.10$ based on the approximation in Eq. (6) are plotted in Fig. 2 and compared to the exact profiles calculated from Eq. (4). In Fig. 2, it is clear that the approximation is quite reasonable, even when the rate constants differ by as much as 30%.

The practical utility of Eq. (6) rests upon the grouping of the less interesting FRS parameters (amplitudes and phase shifts) within the polynomial coefficients $a$, $b$, and $c$. Since these three coefficients appear linearly, fits of FRS data to Eq. (6) should be far less susceptible to the difficulties with nonunique fits encountered with previous regression methods.\textsuperscript{25} Clearly, knowledge of $a$, $b$, and $c$ will not permit evaluation of the parameters $\{\Delta r$, $\Delta \phi$, $A_1$, and $A_2\}$ individually. However, this should not be of practical consequence in most FRS experiments, since the desired quantity is $r_{av}$, which can be obtained in a very direct and unambiguous manner by fitting the data to Eq. (6). This equation is limited to profiles displaying a maximum and a minimum: the approximation can in principle be applied to an arbitrary FRS profile, if one can independently predict on physical grounds that the ratios $r_2/r_1$ and $A_2/A_1$ are not very different from unity, and that $\Delta \phi \ll 1$ rad. It should also be kept in mind that, since Eq. (6) is based on an expansion about the time $t=t_0$, the approximation will break down at very long times.

Examples of fits of the experimental 633 and 543 nm profiles to Eq. (6) for the EtOH and 2-PrOH solvents are shown in Fig. 1. The average rate constants obtained from fitting all experimental profiles at 633 and 543 nm to Eq. (6) are shown as a function of $q^2$ in Figs. 3 and 4 for 2-PrOH and EtOH, respectively. For both solvents, the average rate constants at 633 and 543 nm are very nearly the same. In Table I we list the diffusion coefficients obtained from the slopes of the graphs in Figs. 3 and 4. From the figures and the table it is clear that, to a precision of 2\%–3\%, the diffusion coefficients measured using the two different probe wavelengths are equal, which is entirely consistent with the mixed-grating hypothesis. For completeness, we also show in Figs. 3 and 4 the rate constants obtained from the reciprocal of the time difference $\Delta t$ between the local minimum and the local maximum, as proposed previously for pure phase gratings.\textsuperscript{42,52} From Table I it is evident that for the 633

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$r_{av} (633 \text{ nm})$</th>
<th>$r_{av} (543 \text{ nm})$</th>
<th>$\Delta t (633 \text{ nm})$</th>
<th>$\Delta t (543 \text{ nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanol</td>
<td>4.77±0.05</td>
<td>4.80±0.06</td>
<td>4.57±0.05</td>
<td>5.5±0.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.7±0.2</td>
<td>7.8±0.1</td>
<td>7.7±0.3</td>
<td>...</td>
</tr>
</tbody>
</table>
nm data, the simplified "time-difference" approach agrees reasonably well with results obtained using Eq. (6); not surprisingly, however, the time-difference method fails when applied to the 543 nm data.

Although it is clear from the discussion above that the phase shift $\Delta \phi$ cannot be obtained from the 543 nm profiles in a unique manner, it is possible to determine approximately the largest possible value for $\Delta \phi$ that is consistent with the data. In Fig. 5 we show the results of fitting a single 543 nm FRS profile to Eq. (4). As expected, the results are not unique, and the figure shows five different parameter sets, all of which give good fits to the data. Nevertheless, it is clear from the figure that the ratio of the rate constants $r_2/r_1$ must increase as the value of $\Delta \phi$ employed for the fit is increased, and if we assume, in keeping with previous studies, that the two rate constants are not very different, then the true $\Delta \phi$ must be small. Thus, even if the rate constants differ by as much as 50%, $\Delta \phi$ will still be only $\sim 0.1$ rad. The experimental conclusion that $\Delta \phi$ is small is consistent with the fact that the cis absorption at 543 nm is weak.

In conclusion, we have submitted results showing that, for MY in 2-ProH and EtOH, the same diffusion coefficient is measured at 633 and 543 nm, which provides strong evidence for the proposal that the difference in profile shapes observed at the two different wavelengths is due to the presence of an amplitude/phase grating mixture (hence, a non-zero $\Delta \phi$) at 543 nm. Such amplitude-phase mixtures should be anticipated whenever the probe beam is partially absorbed by photoproduct or ground-state molecules (or both). We believe furthermore that these results constitute a successful test of the more general FRS analysis method based on Eq. (6); this simpler and more direct approach should be applicable to FRS signals generated either by pure phase gratings or amplitude/phase-grating mixtures. We believe these results will help improve the accuracy of FRS studies and should allow FRS experiments on a wider variety of dye/ fluid systems. The new approach could prove especially helpful in FRS experiments in which the variation of a controlled experimental parameter (such as the probe wavelength, temperature, or solvent condition) results in a change in the amount of probe-beam absorption and (hence) in the relative amplitude/phase grating contributions.

Note added in proof: A FRS heterodyne-detection study of phase and amplitude gratings in spiropyran solutions has recently been published by Terazima [J. Phys. Chem. A 103, 7401 (1999)]. The gratings were probed using a single wavelength (633 nm).

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