

- and R. Pappo, *Prostaglandins*, **10**, 733 (1975).
3. P. W. Collins, *J. Med. Chem.*, **29**, 437 (1986).
 4. (a) P. F. Corey, *Eur. Pat.*, 0,133,450; (b) P. W. Collins, C. J. Jung, and R. Pappo, *Tetrahedron Lett.*, **19**, 3187 (1978); (c) T. Tanaka, A. Hazato, N. Okamura, S. Sugiura, K. Toru, and S. Kurozumi, *Tetrahedron*, **43**, 813 (1987).
 5. E. J. Corey, Ned M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Am. Chem. Soc.*, **91**, 5675 (1969).
 6. (a) W. G. Salmond, M. A. Barta, and J. A. Havens, *J. Org. Chem.*, **43**, 790 (1978); (b) A. P. Kozikowski, R. J. Schmiesing, and K. L. Sorgi, *J. Am. Chem. Soc.*, **102**, 6580 (1980); (c) A. P. Kozikowski, H. Ishida, and Y. Chen, *J. Org. Chem.*, **45**, 3350 (1980); (d) E. J. Corey, H. Niwa, and J. Knolle, *J. Am. Chem. Soc.*, **100**, 1942 (1978).
 7. M. Schlosser, H. B. Tuong, and B. Schaub, *Tetrahedron Lett.*, **26**, 311 (1985).
 8. (a) P. J. Kocienski, B. Lythgoe, and I. Waterhouse, *J.C.S. Perkin I*, 1045 (1980); (b) P. J. Kocienski, *Phosphorus and Sulfur*, **24**, 97 (1985).

Mixed Amplitude and Phase Grating Effect in Forced Rayleigh Scattering

Jungmoon Sung, Taihyun Chang*, Jo Woong Lee†, and Hyungsuk Pak†

Department of Chemistry,
Pohang Institute of Science and Technology,
Pohang 790-600

†Department of Chemistry, College of Natural Sciences,
Seoul National University, Seoul 151-742

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Although the forced Rayleigh scattering (FRS) has recently emerged as a powerful tool for the study of mass diffusion in various media,¹⁻⁹ there still remain some aspects of the technique which seem to deserve further attention. The technique utilizes the diffraction from a transient concentration fringe pattern created by a photo-reaction of appropriate photoprobe. In order for the concentration fringe to diffract the light, the product of the photo-reaction (shifted state) should possess a different optical properties from the unshifted state either in absorptivity (amplitude grating) or in refractive index (phase grating).¹⁰⁻¹² If the transient sinusoidal concentration fringe decays by the Fickian diffusion process, the diffracted optical field decays exponentially following the functional form, $E_d = A \exp(-t/\tau)$.

However, deviations from the single exponential type decay of diffracted signal have often been observed and the deviation is ascribed to the difference in the decay time constants of a pair of complementary gratings which consist of excess optically shifted and unshifted state of the photoprobe.^{5,6,9,12,13} Under this circumstance, the time-varying diffracted intensity has been analyzed by the following model function.

$$I_d(t) = [A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2)]^2 + B \quad (1)$$

where τ_1 and τ_2 are the respective decay time constants of two complementary gratings, B is the baseline, and A_1 and A_2 represent the amplitude of optical fields diffracted from each complementary grating. The negative sign arises from the fact that two gratings are 180° out of phase, but it is only valid for either pure phase (contrast in refractive index) or amplitude (contrast in absorptivity) grating.^{11,12} Otherwise, it is necessary to include one more parameter, i.e., the phase difference between two diffracted optical fields from each grating in order to describe the FRS decay profile.^{3,9,11,12} The amplitude and phase grating contribution to the diffraction was well demonstrated previously in the other type of transient optical grating experiment,¹⁰ however, the mixed grating effect exhibits itself in a somewhat different fashion in FRS.

For an unslanted grating, the coupled-wave theory gives the diffracted optical field, E_d from a weak diffraction grating,^{3,10,11}

$$E_d \propto [-i(\Delta n) + (\Delta k)] \quad (2)$$

where Δn and Δk are the gratings peak-null differences in real and imaginary part of complex refractive index, respectively. Eq. (2) shows that a pure amplitude grating ($\Delta n=0$) introduces no phase shift while light diffracted from a pure phase grating ($\Delta k=0$) is shifted by $-\pi/2$. For an arbitrary grating in the weak grating limit, the phase shift is given by

$$\phi = \sin^{-1} \{ -\Delta n / [(\Delta n)^2 + (\Delta k)^2]^{1/2} \} \quad (3)$$

This phase information is lost in the detection of diffracted light from a single grating by a square-law detector such as a photomultiplier. However, the phase shift leads to a distinct departure from a simple exponential decay when the complementary grating effect is visible. For a mixed amplitude and phase grating, Eq. (1) should be written as

$$I_d(t) = |E_d(t)|^2 \\ = [A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \exp(i\Delta\phi)] \times \\ [A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \exp(-i\Delta\phi)] + B \quad (4)$$

where $\Delta\phi$ is the phase difference between the diffracted optical fields from two complementary gratings, i.e. $\Delta\phi = \pi + (\phi_1 - \phi_2)$. The analysis according to Eq. (4) is not trivial and thus it seems advantageous to choose a photoprobe exhibiting either a pure amplitude or phase grating behavior at the reading beam wavelength. In this case, $\Delta\phi = \pi$, which reduces Eq. (4) to Eq. (1).

So far the phase effect due to the mixed grating has not been considered for the analysis of FRS decay profiles. This is likely due to one of the following reasons; (1) the both shifted and unshifted state of the photoprobes do not show a significant absorption at the wavelength of reading beam so that most of the experiments have been carried out at near pure phase grating limit, e.g., use of He/Ne laser reading beam for most of azobenzene derivatives which absorb negligibly at 632.8 nm wavelength; (2) the decay time constants of complementary gratings (i.e., diffusivities of the shifted and the unshifted states) are the same; (3) the shape of decay profiles is such that it is hard to recognize the existent phase effect. If the effect (3) is operational, analysis of the signal by Eq. (2) could lead to an erroneous result.

As can be seen from the simulation results in Figure 1,

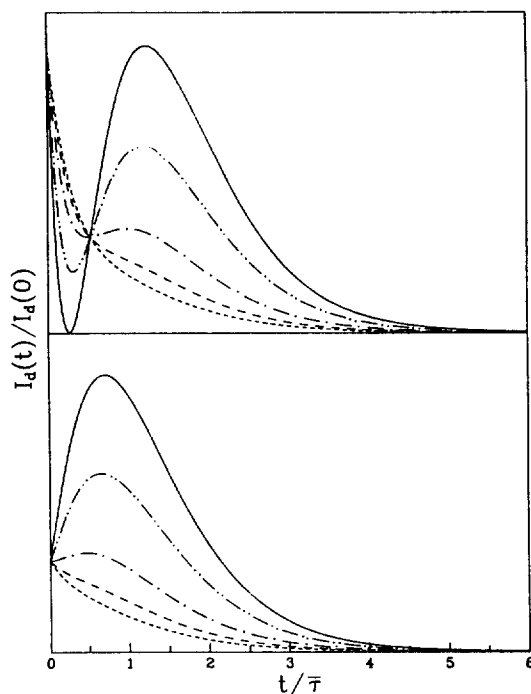


Figure 1. Simulated FRS decay profiles showing how mixed amplitude and phase grating contribution affects the shape of decay profiles for decay-growth-decay type profile (upper plot) and after pulse growth type (lower plot), respectively. They are simulated according to Eq. (4) and relative amplitude of the complementary grating pair is fixed as $A_1/A_2=9.4/8.4$ for easy comparison with ref. 13. The upper plot is for the case of $(\tau_1-\tau_2)/\tau=-0.4$ and the lower one is for $(\tau_1-\tau_2)/\tau=0.4$ where $\tau=(\tau_1-\tau_2)/2$. Each line corresponds to different $\Delta\phi$; $\Delta\phi=180^\circ$ (—), 175° (---), 170° (-·-·-), 165° (-----), and 160° (·····).

the effect is only distinct for a decay-growth-decay type FRS signal (the upper plot, the cases of $A_1>A_2$, $\tau_1<\tau_2$ or $A_1<A_2$, $\tau_1>\tau_2$)^{12,13} where the phase effect is easily discernible from its intensity at the dip position having non-zero values. On the other hand, for the case of after pulse growth type signal (the lower plot, the cases of $A_1>A_2$, $\tau_1>\tau_2$ or $A_1<A_2$, $\tau_1<\tau_2$), the phase effect is not clearly visible. Therefore one should be extremely careful in the analysis of the signal if the probe in either its shifted or unshifted state absorbs the reading beam. Even for the decay-growth-decay type signal, for instance in the report by Rhee *et al.*,³ such phase effect was seemingly not taken into proper account in the analysis.

We close this report by emphasizing the importance of the knowledge on the photochemical properties of chosen probes in order for the correct interpretation of FRS data. It seems to be advantageous for simpler interpretation to choose the experimental condition as either a pure phase or amplitude grating limit. If possible, however, carrying out an experiment at various wavelengths will not only be helpful in deducing correct diffusion coefficients, but also enable us to gain access to other attendant photochemical properties of the system.

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References

1. H. Hervet, L. Leger, and F. Rondelez, *Phys. Rev. Lett.*, **42**, 1861 (1979).
2. H. Kim, T. Chang, J. M. Yohanan, L. Wang, and H. Yu, *Macromolecules*, **19**, 2737 (1986).
3. K. W. Rhee, D. A. Gabriel, and C. S. Johnson, Jr., *J. Phys. Chem.*, **88**, 4010 (1984).
4. M. Antonietti, J. Coutandin, R. Grutter, and H. Sillescu, *Macromolecules*, **17**, 798 (1984).
5. J. Zhang and C. H. Wang, *J. Phys. Chem.*, **90**, 2296 (1986).
6. W. J. Huang, T. S. Frick, M. R. Landry, J. A. Lee, T. P. Lodge, and M. Tirrel, *AIChE J.*, **33**, 573 (1987).
7. Q. Tran-Cong, T. Chang, C. C. Han, and Y. Nishijima, *Polymer*, **29**, 2261 (1988).
8. N. Nemoto, M. Kishine, T. Inoue, and K. Osaki, *Macromolecules*, **23**, 659 (1990).
9. J. Lee, T. Park, J. Sung, S. Park, and T. Chang, *Bull. Korean Chem. Soc.*, **12**, 596 (1991).
10. H. Kogelnik, *Bell Syst. Tech. J.*, **48**, 2909 (1969).
11. K. A. Nelson, R. Casalegno, R. J. D. Miller, and M. D. Fayer, *J. Chem. Phys.*, **77**, 1144 (1982).
12. C. S. Johnson, Jr., *J. Opt. Soc. Am. B*, **2**, 317 (1985).
13. S. Park, J. Sung, H. Kim, and T. Chang, *J. Phys. Chem.*, **95**, 7121 (1991).

Trisilaalkanes; New Precursors for Ultrafine β Silicon Carbide Powders

Gyu-Hwan Lee*, Cheol-Ho Song, and Il Nam Jung*

Organometallic Chemistry Laboratory,
Korea Institute of Science and Technology,
P.O.Box 131, Cheongryang, Seoul 130-650

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Ultrafine silicon carbide powders have been recognized as the material for the high temperature engineering ceramics because of its excellent thermal shock resistance, high-temperature strength and oxidation resistance.¹ These powders are usually prepared by gas phase pyrolysis method of silicon compounds since this method provides many advantages such as high purity, loose aggregation, small particle size, spherical particle shape, and a narrow particle size distribution, suitable for the structural ceramics with the perfection in microstructure.²

Silicon carbide powders have been synthesized by several gas phase processes including plasmas,^{3,4} laser radiation^{5,6} and conventional gas phase reactions in heated furnace tube.^{2,7-9} Though conventional gas phase reaction in the furnace requires high energy, it is regarded as a simple and convenient method for powder synthesis and has advantages of large production rate and capability of using various reactants.

Until now, most of the reactants employed in gas phase