Detection of Minority Species in Microdroplets: Enhancement of Stimulated Raman Scattering

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Spontaneous Raman scattering has served as a useful spectroscopic technique since its discovery. However, the weak signal prevents its application in dynamic environments. Moreover, the Raman spectrum can be overwhelmed by fluorescence from even trace impurities. Stimulated Raman scattering (SRS) is intense, but a minimum sample length is needed to provide the Raman gain. SRS is useful only in detecting majority species because of depletion of the pump laser by the SRS from the strongest-gain Raman mode.

Microdroplets are important constituents of aerosols and sprays, and *in situ* diagnostic techniques are needed to detect minority species in microdroplets. SRS from various liquids has been observed in 10-100 μm microdroplets. The droplet acts as a high-Q cavity ($\approx 10^8$), enhances the Raman gain,[1] and provides feedback for the growth of nonlinear optical processes at wavelengths corresponding to the droplet cavity modes. Pump-laser depletion in droplets is not as significant and SRS from as little as 10% toluene (by volume) in a toluene-pentane mixture has been observed.[2]

By introducing low concentrations of a laser dye into droplets, we have decreased the SRS detectability limit of minority species. Contrary to spontaneous Raman spectroscopy, fluorescence can enhance the stimulated Raman signal generated through Raman amplification of the fluorescence-seeded "noise." Using a tunable dye laser as the pump laser, we can enhance the SRS from a minority species in a binary-mixture droplet by spectrally overlapping the Raman modes of the minority species with the *dissolved* laser-dye fluorescence. When the dye concentration is low (below 10^{-6} M), the initial "noise" photons from the dye fluorescence is much higher than that from the spontaneous Raman scattering of the various solvent Raman modes; hence, the SRS of the minority species becomes preferentially increased. When a higher dye concentration is used (10^{-6} to 10^{-4} M) such that there is a significant amount of dye population inversion, the dye provides additional gain for the buildup of photons at the SRS frequency.[3] The SRS can even act like the seed pulse in an injection-seeded laser, and partially suppresses lasing at other cavity modes at high input-laser intensities.[4] Figure 1 shows a single-shot SRS spectrum from a benzene-dodecane (5% benzene) microdroplet with and without 2×10^{-6} M Rhodamine 560, for an input-laser wavelength of 505 nm. Lasing from Rhodamine 560 occurs in the range of 525-535 nm and overlaps with the 992 cm^{-1} Raman mode of benzene. With fluorescence seeding and gain enhancement from the Rhodamine 560, benzene SRS can be detected at a concentration of as low as 3% benzene.

The Raman gain of minority species can further be increased through resonance Raman enhancement. As an example, we use Rhodamine 6G (R6G) as the minority species to be detected rather than using it as a seeder or "enhancer." We have been able to distinguish[5] resonance SRS of R6G from its own lasing spectrum in droplets with only 2.5×10^{-4} M R6G, because resonance SRS dominates the inelastic emission spectrum at high input-laser intensities at higher R6G concentrations. Dye fluorescence/lasing-gain enhanced SRS, together with resonance Raman enhancement, can thus be useful diagnostic probes for single-shot detection of minority species in sprays.

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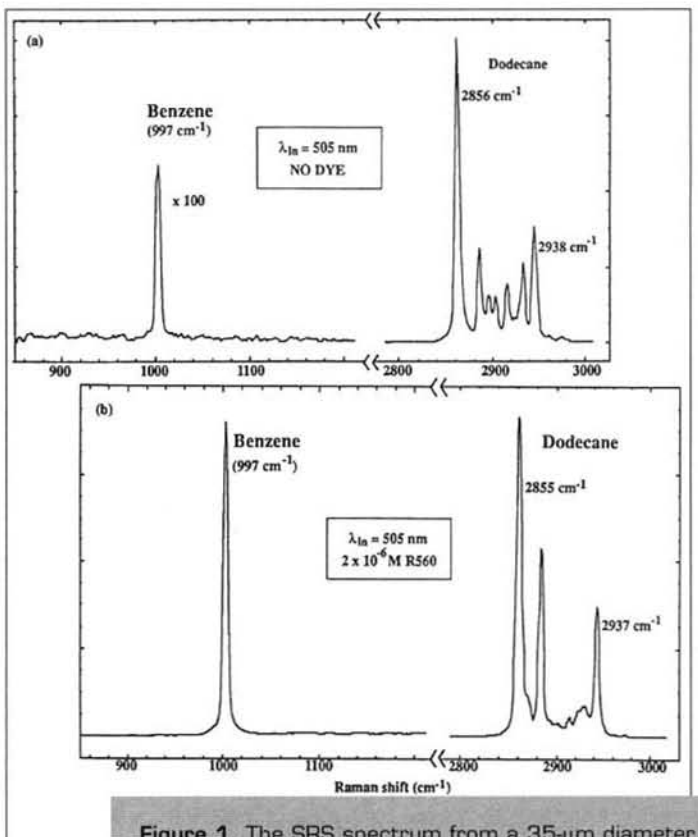

Figure 1. The SRS spectrum from a 35-μm diameter droplet consisting of a mixture of 5% benzene in dodecane (benzene is a precursor to soot formation, and dodecane is a good simultant for a diesel fuel droplet) **(a)** with, and **(b)** without Rhodamine 560. The weak lasing from the Rhodamine 560 overlaps with the 992 cm^{-1} Raman mode of benzene, and enhances the benzene SRS by 100x.