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Addition/Correction

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Correction to “Phase-Matching and Dilution Effects in Two-Dimensional Femtosecond Stimulated Raman Spectroscopy”

Barbara Dunlap, Kristina C. Wilson, and David W. McCamant*

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In our paper, we calculated the phase-matching efficiency of this fifth-order Raman technique for a range of different beam focusing geometries. Those calculations tested the hypothesis that the beam focusing geometry could be optimized to significantly attenuate the third-order cascade, an artifact that dominates the measured signal in 2D-FSRS. In those calculations we calculated the index of refraction for chloroform using coefficients from El-Kashef.[1] However, the El-Kashef indices have been shown to be in disagreement with several other accepted published values, including those measured by Samoc.[2] Here, we show that when the Samoc coefficients for the index of refraction are used in our phase-matching calculations, the different four wave mixing (FWM) processes in 2D-FSRS have higher efficiencies at all of the tested geometries.

Below, we present calculations using Samoc’s coefficients for the index of refraction to correct Figures 6, 7, 8, and 10 of our original publication. Figure numbers match those of the original publication. In general, the correct chloroform refractive index has significantly less dispersion than the index presented by El-Kashef. This produces significantly improved phase-matching at all the explored beam geometries. In our original publication, we discussed the lack of agreement between our experiments and the (incorrect) calculated phase-matching attenuation at large pump crossing angles. In Figure 10, below, one can see that the new calculations fit the observed experimental trends much better than the original calculations. This indicates that the cascade should be strongly attenuated at beam crossing angles much larger than 10°. All of the conclusions from the original paper are still valid, but the effective crossing angle needed to attenuate the cascade signal would need to be larger than originally predicted.

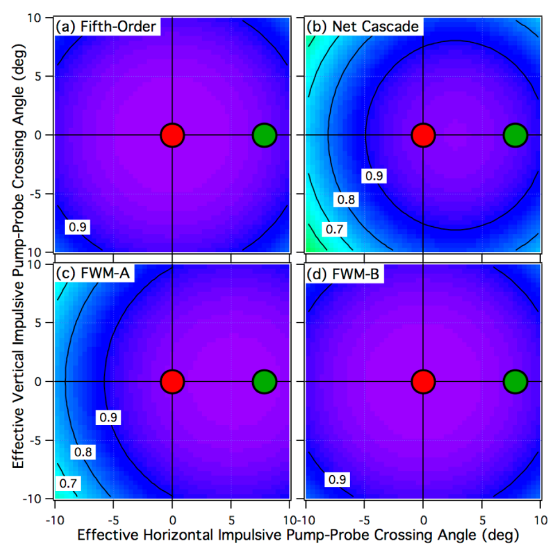

Figure 6. Simulated phase-matching efficiency of the various wave mixing process that can generate the signal at $(\tilde{\nu}_{hi} + \tilde{\nu}_{low})$ = 669 + 262 cm^{-1} sideband. Efficiencies are shown as a function of the position of the impulsive pump (*x* and *y* axes), given that the probe (red dot) is at the origin and the Raman pump (green dot) is at 7.8° to the right (positive crossing angle). (a) Fifth-order signal and (b) net parallel cascade signal. (c) Simulated phase-matching efficiency for the CSRS FWM-A signal and (d) FWM-B, which multiply together to produce the net parallel cascade efficiency shown in (b).

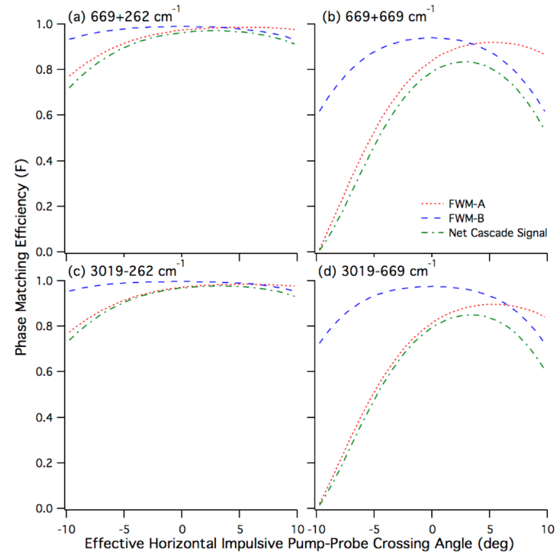

Figure 7. Simulated phase-matching efficiencies of the transitions that create the parallel cascade (green, dot-dashed) as a function of the crossing angle between the impulsive pump and probe. The two transitions making up the cascade are FWM-A (red, dotted) and FWM-B (blue, dashed). Efficiencies are shown for the (a) $(\tilde{\nu}_{hi} + \tilde{\nu}_{low})$ = 669 + 262 cm^{-1} sideband, (b) $(\tilde{\nu}_{hi} + \tilde{\nu}_{low})$ = 669 + 669 cm^{-1} sideband, (c) $(\tilde{\nu}_{hi} - \tilde{\nu}_{low})$ = 3019−262 cm^{-1} sideband, and (d) $(\tilde{\nu}_{hi} - \tilde{\nu}_{low})$ = 3019−669 cm^{-1} sideband. For each calculation, the effective Raman pump−probe crossing angle was held at +7.8°.

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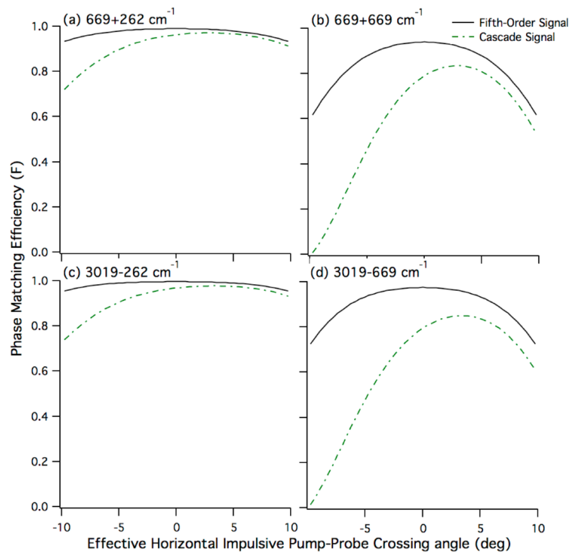

Figure 8. Comparison of the simulated phase-matching efficiency from the fifth-order process (solid black) and parallel cascade (dash-dot, green) as a function of the impulsive and probe crossing angle for the (a) $(\tilde{\nu}_{hi} + \tilde{\nu}_{low})$ = 669 + 262 cm^{-1} sideband, (b) $(\tilde{\nu}_{hi} + \tilde{\nu}_{low})$ = 669 + 669 cm^{-1} sideband, (c) $(\tilde{\nu}_{hi} - \tilde{\nu}_{low})$ = 3019−262 cm^{-1} sideband, and (d) $(\tilde{\nu}_{hi} - \tilde{\nu}_{low})$ = 3019−669 cm^{-1} sideband. For each calculation, the effective Raman pump−probe crossing angle was held at +7.8°.

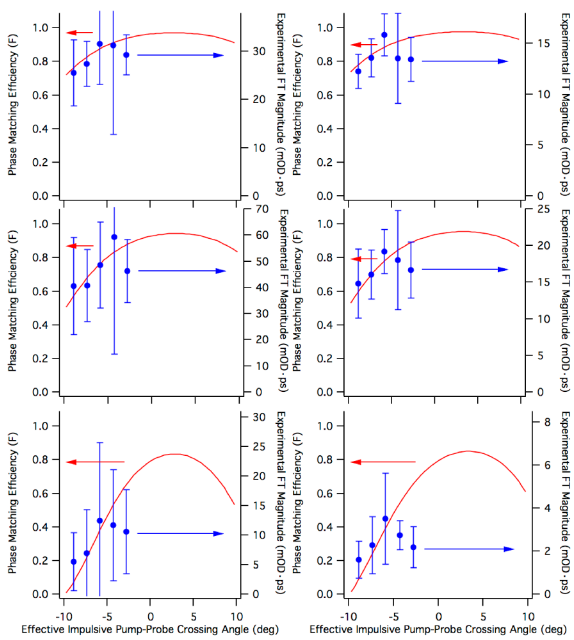

Figure 10. Comparison of theoretical efficiency and experimental intensity of sidebands. Shown are the theoretical efficiency of the parallel cascade signal (red curve, left-hand axis) and experimental FT magnitudes (blue points, right-hand axis) of the peaks upshifted from the 669 cm^{-1} fundamental at the (a) 262 cm^{-1}, (b) 369 cm^{-1}, and (c) 669 cm^{-1} sidebands and downshifted from the 3019 cm^{-1} fundamental at the (a) 262 cm^{-1}, (b) 369 cm^{-1}, and (c) 669 cm^{-1} sidebands.

REFERENCES

(1) El-Kashef, H. *Opt. Mater.* **2002**, *20*, 81−86.
(2) Samoc, A. *J. Appl. Phys.* **2003**, *94*, 6167−6174.