Supporting Information

An Approach to Compatible Multiple Nonlinear Vibrational Spectroscopy Measurements Using Commercial Sum Frequency Generation System

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The IR spectra of riboflavin

FTIR spectra were obtained using a Nicolet 8700 spectrometer. Spectra collected were averages of 32 scans at a 1 cm^{-1} resolution.

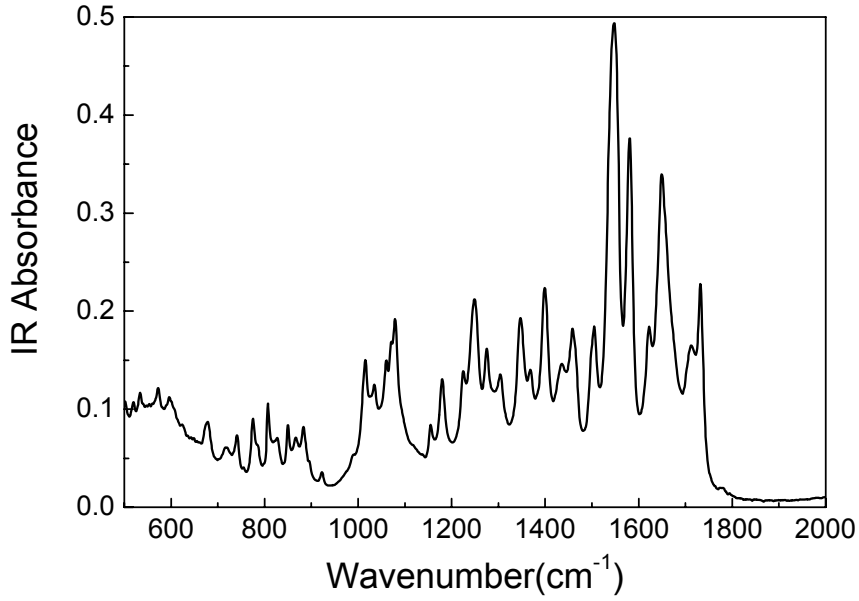

Figure S1. The IR spectra of Riboflavin

The SFG and IIV-TPF-FWM spectra of lumichrome

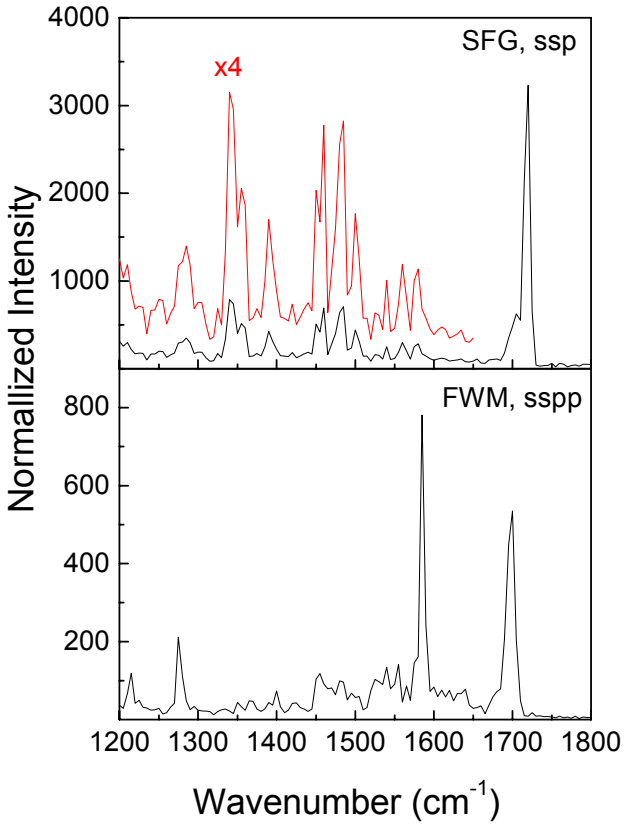

Figure S2. The SFG (ssp) and IIV-TPF-FWM (sspp) spectra of lumichrome

The feasibility to collect DFG spectra using this compatible system

Similar to SFG, DFG is also based on a coherent second-order nonlinear process. The level schemes of the vibrational and electronic configurations involved in DFG process are shown in Figure S3. According to energy and momentum conservation,[1-3] DFG have the following relationships:

$$\omega_{DFG} = \omega_{vis} - \omega_{IR} \quad \text{(S1)}$$

$$\vec{k}_{DFG} = \vec{k}_{vis} - \vec{k}_{IR} \quad \text{(S2)}$$

In the case with an IR beam at 3000 cm^{-1}, DFG will emerge at the angle of 65.31°and the wavelength of 633.17 nm (see Figure S4). The emerging angle is close to the emerging angle of SFG (61.44°) and IIV-TPF-FWM (60.3°). Therefore DFG labview software can be modifiedby controlling the monochromator at ω_{DFG} ($\omega_{DFG} = \omega_{vis} - \omega_{IR}$) when scanning the IR frequency (ω_{IR}).

DFG spectra of riboflavin are given in Figure S5. Similar to SFG, all of the eight polarization combinations have non-vanishing signals. Accepted that the spectra intensity is different, DFG and SFG show the same peak positions. The intensity of DFG spectra is about 5-10% of the intensity of SFG spectra.

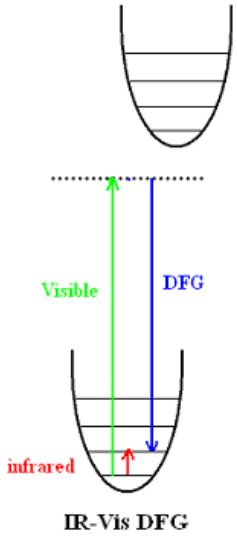

Figure S3. Level schemes of the vibrational and electronic configurations involved in DFG.

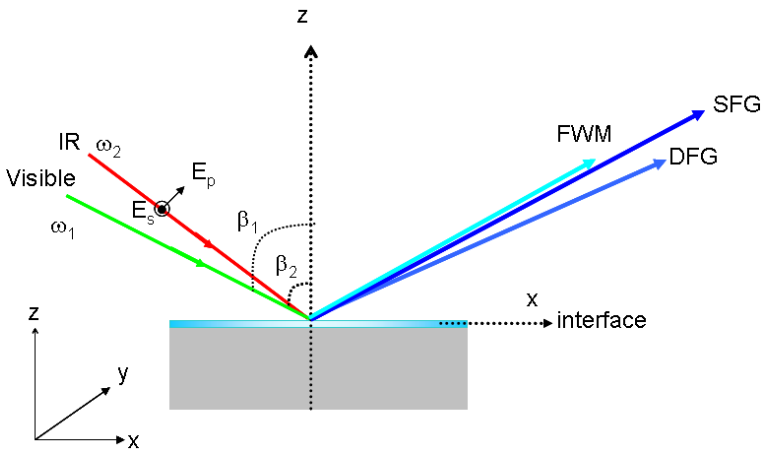

Figure S3. Sketch of the visible and infrared laser beams used to generate the SFG, DFG and FWM signals on the samples.

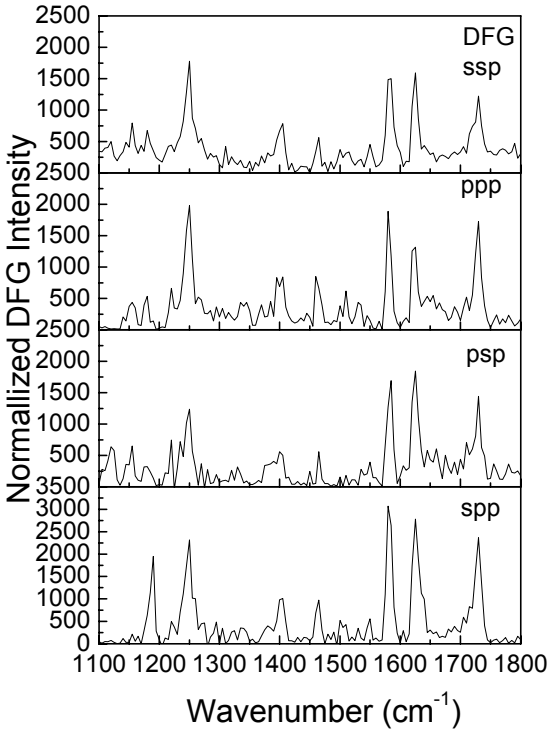

Figure S5. The DFG spectra of (-)-riboflavin.

Reference

1. Y. R.Shen, The Principles of Nonlinear Optics; John Wiley& Sons: New York, 1984.
2. B.Bozzini, A.Bund, B.Busson, C.Humbert, A.Ispas, C.Mele, A.Tadjeddine, *Electrochem. Commun.,* 2010, **12**, 56–60.
3. A.Tadjeddine, A.Le Rille, O.Pluchery, F.Vidal, W.Q.Zheng, A.Peremans, *Phys.Stat.Sol. A,* 1999, **175**, 89-107.