Energy flow between spectral components in 2D broadband stimulated Raman spectroscopy

G. Fumero[1,*], G. Batignani[1,2], S. Mukamel[3] and T. Scopigno[1]

[1]Dipartimento di Fisica, Sapienza, Università di Roma. [2]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila. [3]Department of Chemistry, University of California, Irvine.
[*]giuseppe.fumero@uniroma1.it

We introduce a general theoretical description of non-resonant 2D broadband stimulated Raman spectroscopy in a multimode model. Upon impulsive excitation, coherences induced in the low frequency modes modulate the Raman signal in time. Monitoring the transmitted intensity, we elucidate the mechanism underlying the energy redistribution pathway between probe field modes.

Ultrafast coherent Raman spectroscopy is a fundamental tool in scientific inquiry, due to its capability to reach picosecond and sub-picosecond time scales at which molecular systems evolve. Its multidimensional implementation allows for the time resolved characterization of harmonic and anharmonic couplings between vibrational degrees of freedom, during optically and chemically induced structural modifications in molecules [1, 2]. The investigation of such effects, however, implies deciphering complex signals and a careful modeling is required in order to extract the information brought by the experimental measurements.

To this aim, we employ a microscopic diagrammatic approach to broadband stimulated Raman spectroscopy with an impulsive off-resonant actinic pump [3]. In this technique, an ultrashort actinic pump creates coherences of low frequency modes that are probed by the joint action of a narrowband Raman pulse and a broadband probe pulse, via stimulated Raman scattering through an higher frequency mode. Using loop diagrams, the complete response of the system is calculated at the relevant perturbation order. We show that coherences created by the impulsive pump modify the resulting Raman signal, which oscillates from gain to loss features, depending on the time delay between the pump and probe pulses. The interplay of these features is responsible for a redistribution of photons between the red and the blue sides of the broadband pulse with respect to the narrowband Raman pulse. The total number of photons is conserved but the energy flows between fields and matter (Fig. 1).

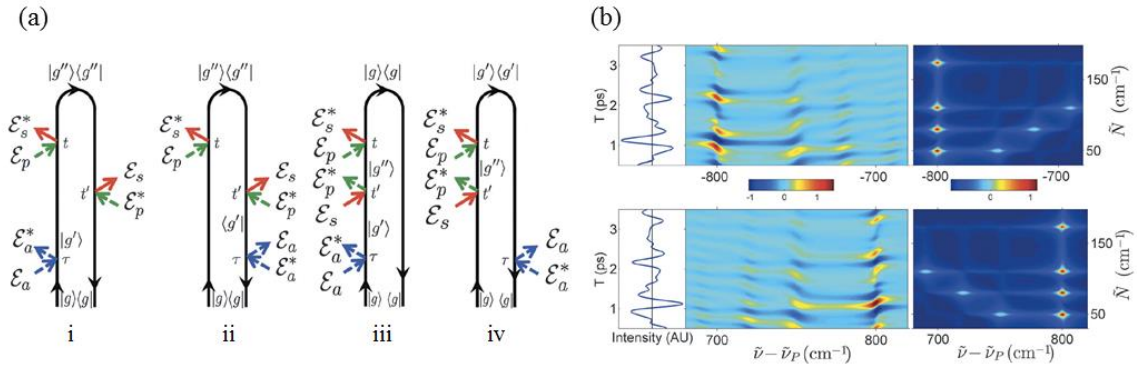

Fig. 1 (a) Closed-time-path-loop diagrams for stimulated Raman with an impulsive actinic pump preceding the probe fields, under off-resonance conditions. (b) Time delay dependent 2D signal (central panel) and its Fourier Transform (right panel) for diagrams i-ii (top) and for diagrams iii-iv (bottom); the response is calculated for a system with four low frequency modes and one high frequency mode, using an 80 fs actinic pump. System parameters are given in [3]. The number of probe pulse photons for the red and blue side of the spectrum is reproduced in the left panel.

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