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Supplementary Infromation: Energy flow between spectral components in 2D Broadband Stimulated Raman Spectroscopy

G. Batignani[a,b], **G. Fumero**[a], **S. Mukamel**[c] **and T. Scopigno**[a,d*]

a Dipartimento di Fisica, Universitá di Roma "Sapienza", I-00185 Roma (Italy).
b Dipartimento di Scienze Fisiche e Chimiche, Universitá degli Studi dell'Aquila , I-67100, L'Aquila (Italy).
c Department of Chemistry, University of California, Irvine, California 92697-2025 (USA).
d Centre for Life Nano Science – IIT@Sapienza, Istituto Italiano di Tecnologia, I-00161 Roma (Italy).

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Supplementary Material

The detected signals can be directly derived from the CTPL diagrams by the use of the following rules:

1. Time runs clockwise along the loop from the bottom left to the bottom right.
2. The interactions within each branch are time ordered, but interactions on different branches are not. Each loop can be further decomposed into several fully-time-ordered diagrams (double-sided Feynman diagrams).
3. A field mode is represented by an arrow.
4. The loop contains a series of interactions, depicted as intersection between the loop and the arrows. Interactions are separated by periods of free evolutions s_i, forwards in real time on the left branch and backwards on the right branch.
5. Arrows pointing to the right represent interaction with the field annihilation operator $\mathcal{E}_j(\omega)$, while arrows pointing to the left represent interaction with the field creation operator $\mathcal{E}_j^\dagger(\omega)$. The interactions are with a couple of arrows $\mathcal{E}_i\mathcal{E}_j^\dagger$ and are accompanied by the polarizability α.
6. For each period of free evolution on the left branch we write a retarded Green's function $G(\sum_j \omega_j)$, where the sum goes over all earlier interactions along the loop, i.e. the frequency arguments of the various propagators are cumulative; additionally, the ground state frequency ω_g is added to all arguments of the propagators. Similarly for each period of free evolution on the right branch we write an advanced Green's function $G^\dagger(\sum_j \omega_j)$.
7. The interaction at the observation time t is fixed to be with the detected mode and is always the last. It is chosen to be on the left branch of the loop.
8. The overall sign of the correlation function is given by $(-1)^{N_{int}}$, where N_{int} is the number of interactions along the loop, i.e. the number of intersections between the loop and the arrows.
9. Signal expression contains a delta function $2\pi\,\delta(\sum_{j=1}^{n+1} \omega_j)$, accounting for energy conservation.

Loop diagrams of Fig. 1 can be recasted in term of Double-Sided Feynman or energy level diagrams. For example in Fig. S1 we present the energy level diagrams which correspond to the term i of Fig. 1, producing contributions at $\omega_P - (\omega_h - \omega_l)$ and $\omega_P - \omega_h$.

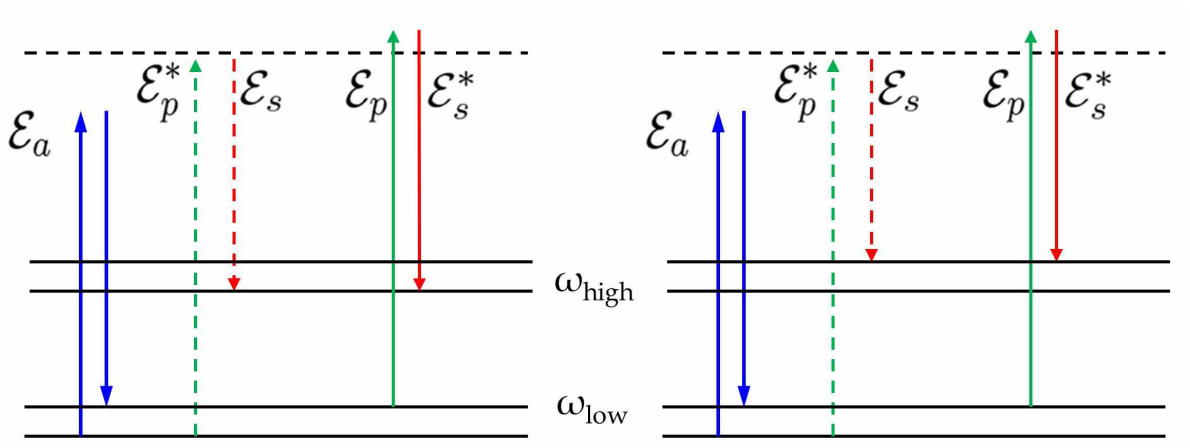

Fig. S1: Energy-level diagrams corresponding to term *i* of Fig. 1.

In Fig. S3 we provide a quantitative comparison with some previous theoretical treatments of Lee [19], where the fifth-order response of a $CDCl_3$ molecule is calculated; here we verify that our results can be simply applied to the systems studied by Lee and that the general harmonic potential used in our paper guarantees phase conservation for the sidebands associated to the same low frequency mode, while the anharmonic potential can produce a 180 degrees shift of the relative phases.

References

1 Z. Sun, B. Fu, D. H. Zhang and S.-Y. Lee, *J. Chem. Phys.*, 2009, **130**, 044312.

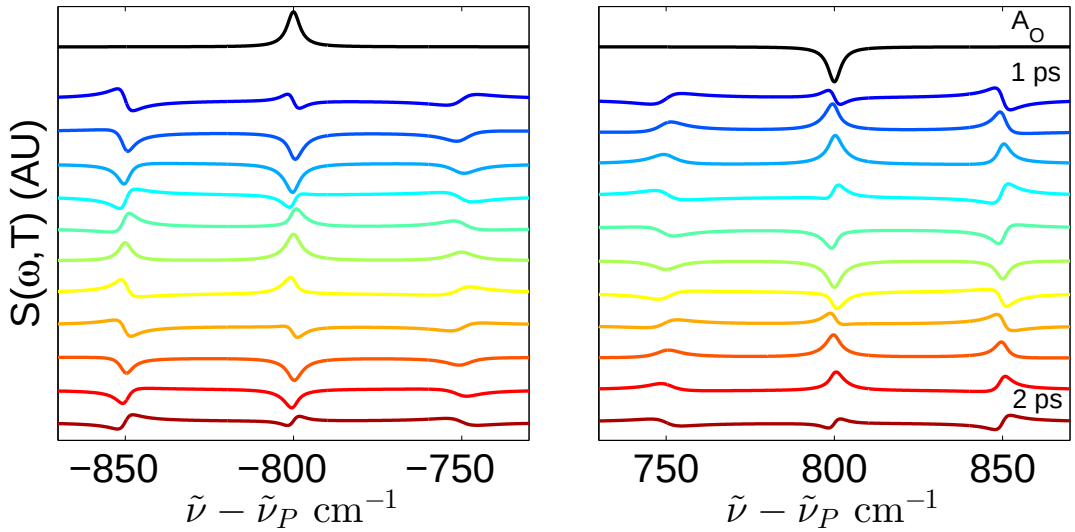

Fig. S2: Slices of Fig. 2 signal at different time delays, from 1 ps to 2 ps in steps of 100 fs, are reproduced and compared to the third order (normalized) response of the system without the actinic impulsive excitation, reproduced by the black line.

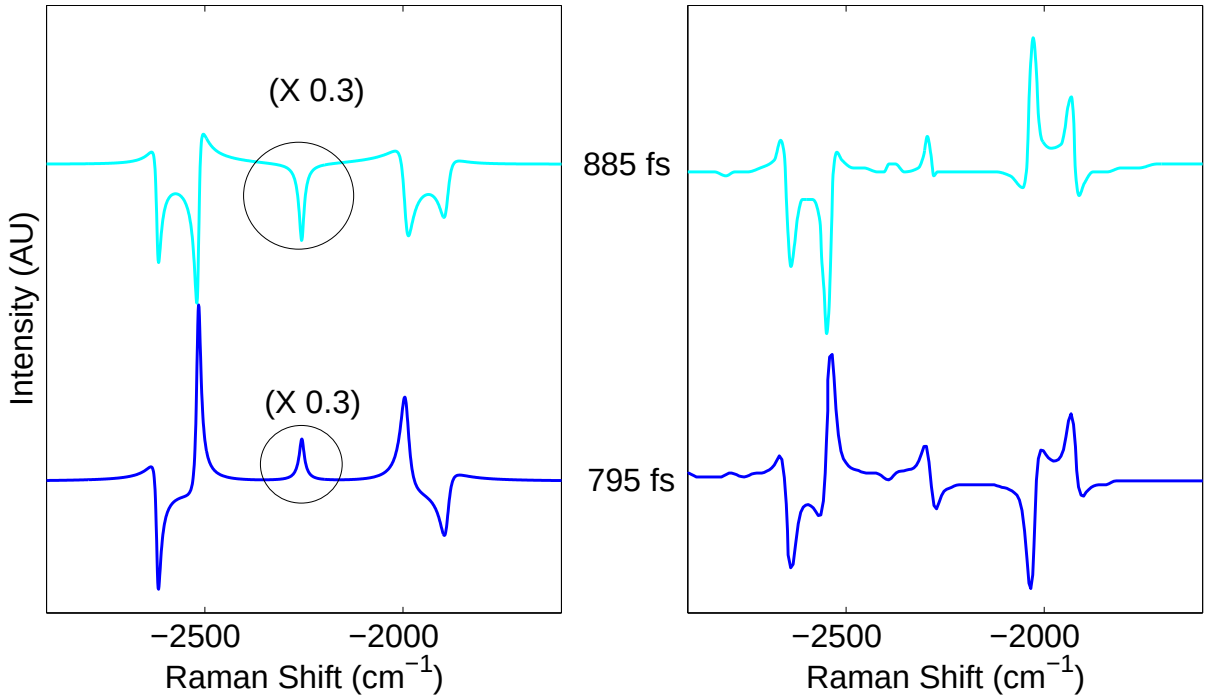

Fig. S3: Comparison between our results (reduced to the red side of the spectrum on the left panel) and the ones obtained in [19] by Lee et al. (reproduced on the right panel for the red side of the spectrum), where the fifth-order response of a $CDCl_3$ molecule with an high frequency mode at $2255\,\mathrm{cm}^{-1}$ and two low frequency modes at respectively $262\,\mathrm{cm}^{-1}$ and $365\,\mathrm{cm}^{-1}$. The work of Lee considers an anharmonic potential, which produces a 180 degrees relative phase modification of the sidebands, while the harmonic potential used in our work guarantees phase conservation for sidebands associated to the same low frequency modes.