Single-pulse Two-dimensional Raman Spectroscopy

Hadas Frostig[1], Tim Bayer[1], Nirit Dudovich[1], Yonina C. Eldar[2] and Yaron Silberberg[1]
[1]*Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel.*
[2]*Department of Electrical Engineering, Technion, Haifa 32000, Israel.*
Hadas.Frostig@weizmann.ac.il

We present a single-pulse two-dimensional Raman spectroscopy scheme. Our scheme offers not only a major simplification of the conventional setup but also an inherent favoring of the direct fifth-order signal over the cascaded signal, the latter being a signal that carries no coupling information.
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Understanding the structure of complex molecular systems and following their evolution during chemical and biological processes are central issues in chemical physics and biophysics. Fifth-order 2D impulsive Raman spectroscopy can be used to probe the molecular structure, as in 2D nuclear magnetic resonance (NMR) spectroscopy, but on an ultrafast time scale [1]. As a result, this method attracted a lot of interest when introduced [2,3]. The conventional scheme makes use of five femtosecond pulses in a non-collinear geometry. The pulses arrive at three distinct times to the sample and consecutively excite, couple and probe vibrational levels via impulsive Raman processes (see fig. 1(a)). However, from the start, the use of 2D Raman spectroscopy was hindered by unwanted lower-order cascade signals, which often overwhelmed the desired signal completely and did not carry any structural information [3,4]. This difficulty, together with the complex multi-beam setup required, prevented this method from living up to the initial expectations and becoming widely used and applied in biophysics research.

Here we present a scheme that uses coherent control techniques [5], to excite and probe this entire process with a single femtosecond pulse. The experimental apparatus requires only a pulse shaper and a simple detection system (see fig. 1(b)). The shaper is used to apply a spectral phase mask that is the sum of two periodic phase functions with periods Ω_{01} and Ω_{12}. The resulting pulse sequence in time domain is a convolution of two trains, one with a delay $\tau_{01}=2\pi/\Omega_{01}$ and another with a delay $\tau_{12}=2\pi/\Omega_{12}$. τ_{01} trains selectively excite molecules from the ground state to a vibrational level ω_1 whereas τ_{12} trains selectively couple from level ω_1 to another vibrational level ω_2. Our detection relays on the fact that stimulated Raman scattering of a broadband pulse causes a spectral shift of its output spectrum [6]. Thus, to perform 2D spectroscopy, the two modulation periods are scanned while the spectral shift value of the output spectrum is recorded. The resulting 2D data is Fourier-transformed.

In addition to considerably simplifying the setup, our use of collinear geometry, together with spectrally-resolved detection, makes our scheme inherently insensitive to the cascade signal. Due to the collinearity, the field detected after the sample is in fact the coherent interference of the field going into the sample, E_{in}, with the fifth-order field, $E^{(5)}$, generated in the sample. Since $E_{in}>> E^{(5)}$, $E^{(5)}$ serves, in practice, as a local oscillator that amplifies the component of the $E^{(5)}$ that is in-phase with it, typically by several orders of magnitude.

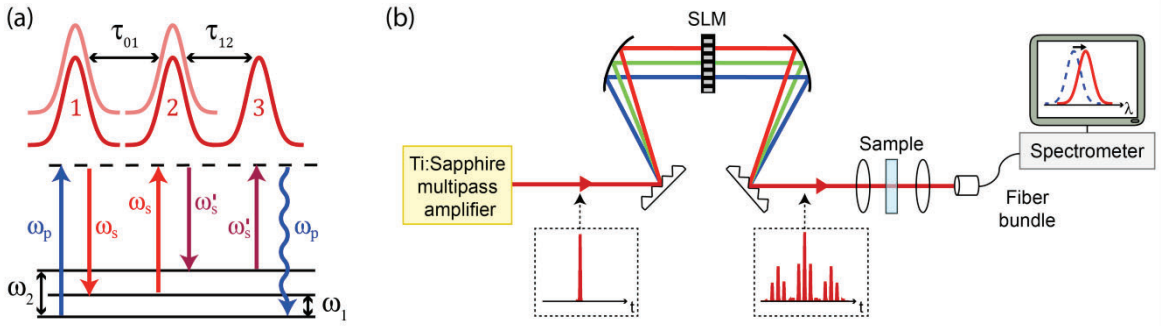

Fig. 1: (a) Energy diagram of the fifth-order Raman process. Conventionally this process is excited with the pulse sequence shown above, comprised of five pulses in non-collinear geometry. The pulses arrive at three distinct times to the sample causing mode excitation, mode-to-mode coupling, and probing of the vibrational levels respectively. (b) A schematic of the setup of our 2D Raman spectroscopy method, which uses a single pulse to excite the entire fifth-order process. The pulses are phase-shaped using a spatial-light modulator and then focused onto the liquid samples. The spectral shift of the transmitted light is measured with a spectrometer.

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Therefore, for a real E_{in}, only the real parts of both the direct field, $E_{dir}^{(5)}$, and the cascade field, $E_{cas}^{(5)}$, are detected. In addition, our use of spectral shift detection filters out any components of $E^{(5)}$ that are spectrally symmetric and will not cause a shift when interfered with E_{in}. Because the field radiated by the direct fifth-order polarization undergoes one radiation event whereas the field radiated by the cascaded third-order polarization undergoes two such events, $E_{cas}^{(5)}$ and $E_{dir}^{(5)}$ are identical except their real and imaginary parts are swapped. While the in-phase component of $E_{dir}^{(5)}$ is antisymmetric and therefore causes a blueshift when combined with the stronger E_{in}, the in-phase component of $E_{cas}^{(5)}$ is spectrally symmetric, and therefore leaves the spectrum unshifted. Consequently, spectral shifts are insensitive to the cascade signal.

The single-pulse 2D Raman spectra of several liquid samples are shown in Fig. 2. In all three samples, strong peaks corresponding to the 1D data are present on the diagonal. Off the diagonal, several cross peaks are clearly visible, in both the 2D spectra of CCl_4 and of $CHCl_3$ (Fig. 2(a) and (b) respectively) indicating coupling between the corresponding vibrational levels. We also observe off-diagonal peaks of each mode with its overtones and undertones which are caused by the 1D $E^{(3)}$ signal. In order to test whether the scheme is truly insensitive to the cascade signal, we measured the 2D spectrum of a CCl_4:$CHCl_3$ mixture at a 1:1 mole ratio. The result is presented in Fig. 2(c). We note that the cross peaks between modes of the same molecule are present whereas the cross peaks between modes of the two different molecule species are not observed. This result indicates that the signal that our scheme measures does in fact originate from intramolecular coupling.

[1] Okumura, K., Tokmakoff, A., and Tanimura, Y., "Structural information from two-dimensional fifth-order Raman spectroscopy", J. Chem. Phys. **111**(2), 492-503 (1999).

[2] Tokmakoff, A., Lang, M. J., Larsen, D. S., and Fleming G. R., "Two-Dimensional Raman Spectroscopy of Vibrational Interactions in Liquids", Phys. Rev. Lett. **79**(14), 2702-2705 (1997).

[3] Blank, D. A., Kaufman, L. J., and Fleming, G. R., "Direct fifth-order electronically nonresonant Raman scattering from CS2 at room temperature", J. Chem. Phys. **111**(7), 3105-3114 (1999).

[4] Wilson, K. C., Lyons, B., Mehlenbacher, R., Sabatini, R., and McCamant, D. W., "Two-dimensional femtosecond stimulated Raman spectroscopy: Observation of cascading Raman signals in acetonitrile", J. Chem. Phys. **131**(21), 214502 (2009).

[5] Dudovich, N., Oron, D., and Silberberg, Y., "Single-pulse coherently controlled nonlinear Raman spectroscopy and microscopy", Nature **418**(6897), 512-514 (2002).

[6] Frostig, H., Katz, O., Natan, A., and Silberberg, Y., "Single-pulse stimulated Raman scattering spectroscopy", Opt. Lett. **36**(7), 1248-1250 (2011).

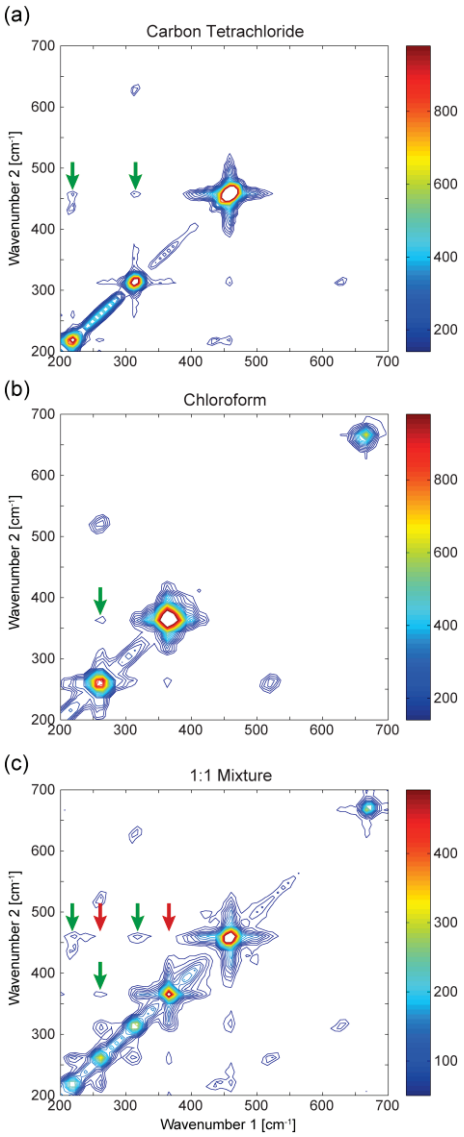

Figure 2: Results from 2D single-pulse Raman spectroscopy of several samples. (a) The 2D spectrum of CCl_4. In addition to the strong diagonal peaks, cross peaks between the 459cm^{-1} and 217cm^{-1} modes and between the 459cm^{-1} and 313cm^{-1} modes are observed (marked with arrows). (b) The 2D spectrum of $CHCl_3$. Some coupling is observed between the 263cm^{-1} and 369cm^{-1} modes. (c) The 2D spectrum of a 1:1 mole ratio CCl_4:$CHCl_3$ mixture. Significant cross peak are observed between the modes of the same molecule (marked with green arrows), such as between the 313cm^{-1} and the 459cm^{-1} modes of CCl_4, but not between the modes of different molecules (locations marked with red arrows), such as between the 459cm^{-1} mode of CCl_4 and the 369cm^{-1} mode of $CHCl_3$.