# Signatures of Conical Intersection Mediated Relaxation Dynamics in Time-Resolved Broadband Raman Detection

**Benjamin P. Fingerhut, Konstantin E. Dorfman and Shaul Mukamel**

**Abstract** Ab-Initio simulations of Raman signals reveal the excited state deactivation mechanism of uracil. The signals provide sub-molecular sensitivity of out-of-plane displacements during conical intersection mediated relaxation and properly describe the time-resolution of the techniques.

## 1 Ultrafast Relaxation Dynamics of RNA and DNA Bases

The strong UV absorption bands of DNA and RNA nucleobases lead to the population of bright valence excited states with $\pi\pi^*$ character. The nucleobases have been engineered by nature to be photostable with respect to UV irradiation. At the core of this self-protecting property are ultrafast excited-state deactivation mechanisms involving conical intersections where electronic energy is very rapidly converted into vibrational energy, allowing to minimize harmful photochemical processes that can eventually lead to DNA photolesions. Two relaxation paths have been proposed for pyrimidine bases, one being an ultrafast direct $\pi\pi^* \rightarrow$ ground state (gs) channel, the other one involves relaxation into a dark $n_O\pi^*$ state. The access to the conical intersection seams of either channel determines the excited-state lifetime and deactivation mechanism of the pyrimidine bases.

Structural information about the required rearrangements of atoms can be derived directly from time- and frequency-resolved vibrational spectroscopy with Raman probes. Here we demonstrate that the high-frequency modes of uracil serve as sensitive fingerprints of the excited-state photoreaction and the associated non-adiabatic relaxation dynamics. Transient out-of-plane deformations of the $\pi$-ring

B.P. Fingerhut (✉)
Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, 12489 Berlin, Germany
e-mail: fingerhut@mbi-berlin.de

K.E. Dorfman · S. Mukamel
Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

system can be monitored and mapped on characteristic dispersive features reflecting the local molecular changes of involved conical intersection structures.

## 2 Off-Resonant Raman Detection Schemes

We consider different off-resonant Raman techniques (i.e. the homodyne-detected frequency-resolved spontaneous Raman signal (FR-SPRS), heterodyne-detected time-resolved impulsive stimulated Raman signal (TR-ISRS), transient grating impulsive stimulated Raman signal (TG-ISRS), and femtosecond stimulated Raman signal (FSRS)) which provide information about the same four-point matter correlation functions:

$$F_i(t_1, t_2, t_3) = \left\langle VG^\dagger(t_1)\alpha G^\dagger(t_2)\alpha G(t_3)V^\dagger \right\rangle, \qquad (1)$$

$$F_{ii}(t_1, t_2, t_3) = \left\langle VG^\dagger(t_1)\alpha G(t_2)\alpha G(t_3)V^\dagger \right\rangle. \qquad (2)$$

They contain all relevant information about the matter, but with different detection windows. In FSRS, TR-ISRS, and TG-ISRS the symmetry between the both branches of the loop diagram is broken (see Fig. 1), which explains microscopically the origin of dispersive peak shapes. In FR-SPRS the signals can be recast as a modulus square of the transition amplitude and only absorptive lineshapes appear [1].

The different time-resolved Raman signals are simulated within a recently developed semi-classical simulation protocol [2, 3], which treats nuclear motions classically but fully retains the quantum character of electrons thus allowing to follow the complex dynamics over conical intersections on CASSCF (14/10) level of theory. The excited state instantaneous frequencies of spectator modes (Fig. 2a), modulated in the classical bath of remaining modes, are reconstructed in a mode tracking procedure which decouples the numerical effort from system size. The signal expressions contain a path integral over the excited state instantaneous frequencies and thus properly describe the time-resolution of the techniques.

## 3 Time-Resolved Raman Signatures of Conical Intersection Mediated Relaxation of Uracil

The simulated excited state dynamics of uracil is characterized by ultrafast population redistribution (after $\sim 190$ fs), where the bright $S_2$ state ($\pi\pi^*$ character) is depopulated and serves as a reservoir for both relaxation channels ($\pi\pi^* \rightarrow$ gs channel and dark $n_O\pi^*$ state population). The derived $\pi\pi^*$ lifetime is 516 fs (single exponential fit) which is in good agreement with the 530 fs time constant reported by Ullrich et al. [4]. The molecular changes of involved conical intersection structures
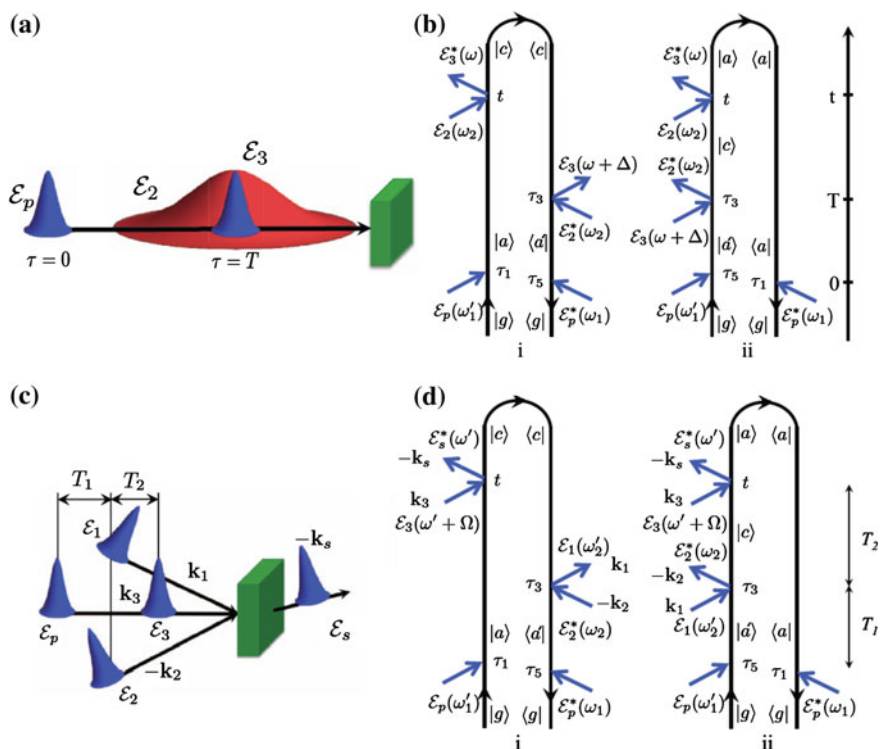
**Fig. 1** Schematic layout and loop diagrams of the FSRS (**a**, **b**) and the TG-ISRS (**c**, **d**) technique: in FSRS pulse $E_p$ initiates the vibrational excited state dynamics. The Raman probe sequence consists of a picosecond $E_2$ and a femtosecond pulse $E_3$, the signal is given by frequency-dispersed probe transmission $E_3(\omega)$. In TG-ISRS, two short pulses ($\mathbf{k_1}$ and $\mathbf{k_2}$) coincide after a delay $T_1$ and form an interference pattern with wave vector $\mathbf{k_1} - \mathbf{k_2}$. After a second delay period $T_2$, a third beam with wave vector $\mathbf{k_3}$ is scattered off the grating to generate a signal with wave vector $\mathbf{k_S} = \mathbf{k_1} - \mathbf{k_2} + \mathbf{k_3}$

are characterized by an out-of-plane deformation of the pyrimidine $\pi$ system (see inlay in Fig. 2b) which instantaneously modifies the local potential of high-frequency C–H spectator modes (see Fig. 2a for the $\pi\pi^* \rightarrow$ gs channel).

Analysis of the joint time/frequency resolution of the Raman techniques is provided on the basis of the $\Delta$-dispersed signal (Fig. 2b). Even though not an experimental observable, the $\Delta$-dispersed signal contains all matter contributions to off-resonant Raman probes where the dispersion in the $\Delta$-axis reveals the inherent matter chirp contributions that limit the temporal resolution of the techniques but determine the required probe pulse bandwidth.

Figure 2c depicts the FSRS signal of the direct $\pi\pi^* \rightarrow$ gs relaxation mechanism of uracil which is initially characterized by a single, system dynamics broadened resonance. Due to the non-adiabatic relaxation induced frequency shift the resonance evolves toward $\omega - \omega_3 = 3{,}100 \text{ cm}^{-1}$ with complex dispersive line shape
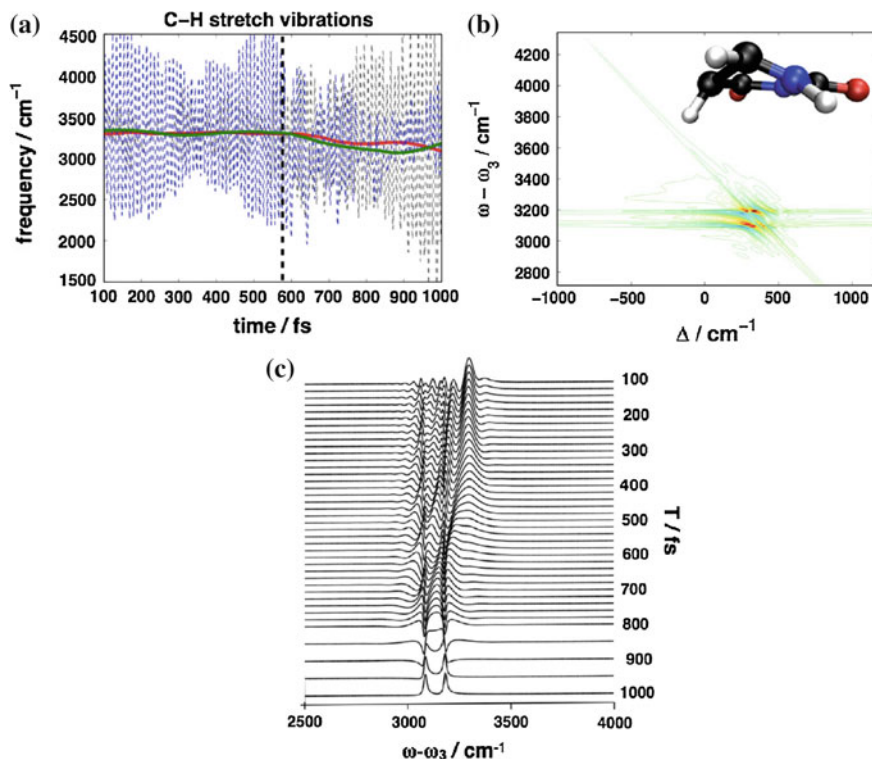
**Fig. 2** **a** Instantaneous frequencies, **b** Δ-dispersed signal for T = 586 fs and **c** FSRS signal of C–H stretch vibrations of the direct $\pi\pi^* \rightarrow$ gs relaxation mechanism of uracil. Dispersive features in FSRS detection are induced by passage through conical intersection structures shown as inlay. The required bandwidth is represented in the Δ-axis of **b**

(T > 550 fs). As the delay time $T$ and the frequency resolution of the detection axis $\omega - \omega_3$ are independent experimental knobs, the FSRS signal at time $T$ does not represent a snapshot of the system dynamics. Resonances appear broadened due to the matter dynamics induced chirp contribution which modulates line-shapes and induces the dispersive features in the FSRS signals. These reflect the partial re-hybridization pattern of the displaced carbon atoms and also survive ensemble averaging. TG-ISRS and TR-ISRS allow the manipulation of both, the pump and probe pulses. In the limit of ultrashort pump TG-ISRS/TR-ISRS provide the same resolution as FSRS.

# References

1. K. E. Dorfman, B. P. Fingerhut, and S. Mukamel, "Time-resolved broadband Raman spectroscopies: A unified six-wave-mixing representation", J. Chem. Phys. **139**, 124113 (2013).
2. K. E. Dorfman, B. P. Fingerhut and S. Mukamel, "Broadband infrared and Raman probes of excited-state vibrational molecular dynamics: simulation protocols based on loop diagrams", PCCP **15**, 12348-12359 (2013).
3. B. P. Fingerhut, K. E. Dorfman and S. Mukamel, "Probing the Conical Intersection Dynamics of the RNA Base Uracil by UV-Pump Stimulated-Raman-Probe Signals; Ab Initio Simulations", J. Chem. Theory Comput. **10**, 1172–1188 (2014).
4. S. Ullrich, T. Schultz, M. Z. Zgierski and A. Stolow, "Electronic relaxation dynamics in DNA and RNA bases studied by time-resolved photoelectron spectroscopy Phase-coherent generation of tunable visible femtosecond pulses", PCCP **6**, 2796–2801 (2004).