

Transient 2DIR spectroscopy in a vibrational ladder

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Abstract We perform transient two-dimensional Fourier-Transform infrared spectroscopy after vibrational ladder climbing in carboxy-hemoglobin. We will discuss how the observed diagonal and cross-peak dynamics can be related to population relaxation in this non-stationary system brought far from equilibrium.

We perform transient two-dimensional infrared spectroscopy (t-2DIR) [1] on the CO stretching mode of carboxy-hemoglobin initially prepared far from equilibrium by use of vibrational ladder climbing [2]. As shown in Fig. 1(a), the pulse sequence includes an intense mid-IR chirped pump, which prepares a non-equilibrium vibrational population distribution as schematized in Fig. 1(b). Three transform-limited mid-IR pulses are then used for the Fourier-transform 2DIR measurement, performed here in the pump-probe geometry [3]. Fig. 2 shows a series of t-2DIR spectra recorded for several values of the waiting time T . Several vibrational levels being simultaneously populated, the t-2DIR spectra exhibit a large number of peaks arranged on a square grid. Thanks to vibrational anharmonicity, each peak can be assigned to the corresponding transitions induced by the 2D pump and probe pulses. For a vanishing waiting time, a series of three peaks is expected for every resonant pump frequency. Note in particular the positive peaks just right of the diagonal, corresponding to the induced

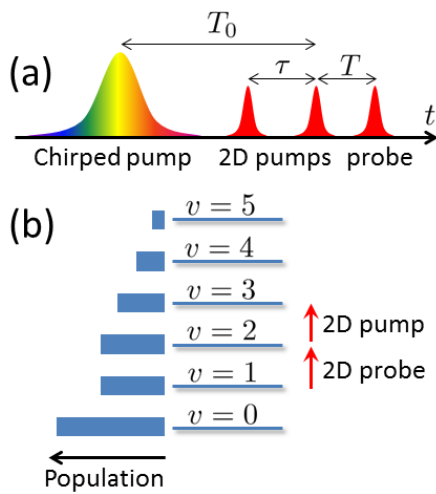


Fig. 1 (a) Pulse sequence. (b) Typical vibrational population at a time T_0 after ladder climbing induced by the chirped pump pulse.

absorption seen by the probe after depletion of the upper level by the 2D pump (see associated transitions in Fig. 1(b) and dotted circle in Fig. 2). Vibrational relaxation during the waiting times yields a rich dynamics: the first peaks right of the diagonal change sign, and additional weaker peaks appear further right, in good agreement with numerical simulations.

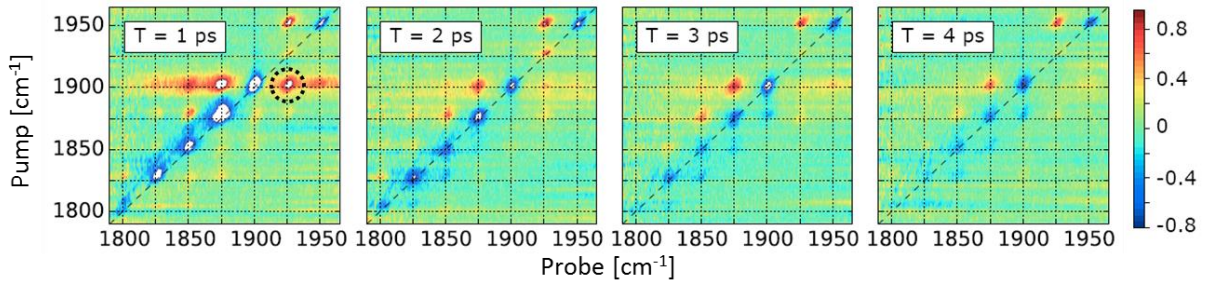


Fig. 2. Series of t-2DIR spectra recorded for different values of the waiting time T , for a system prepared out of equilibrium by vibrational ladder climbing achieved using an intense chirped pulse applied 18 ps before the second 2D pump pulse. The circled cross peak at $T = 1$ ps corresponds to the process shown in Fig. 1(b).

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- [3] L. P. DeFlores *et al.*, *Opt. Lett.* **32**, 2966 (2007).