VIPER 2D-IR: A Novel Pulse Sequence to Track Exchange Beyond the Vibrational Lifetime

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Abstract: We present a new IR/UV-VIS pulse sequence that uses an IR pulse to pick a molecule within a mixture, in order to monitor its photochemistry. The benefits of this sequence over commonly used ones discussed.
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1. Mixed IR/Vis 2D Spectroscopies

The rich possibilities of 2D-IR spectroscopy can be even further enhanced by incorporating Vis or UV pulses in the IR pulse sequence. Several mixed ultrafast IR/Vis pulse sequences have been developed so far, each having its specific applications. Transient 2D-IR spectroscopy takes 2D-IR spectra of populations that are photoactivated by a Vis pulse preceding the 2D-IR pulses [1]. In non-equilibrium 2D-IR exchange spectroscopy (2D-IR EXSY, also termed triggered exchange spectroscopy), a resonant UV/Vis pulse is applied during the population time of the 2D-IR experiment. In this way cross peaks are generated that correlate the vibrations of the transient species with the vibrations of the starting state [2]. Another pulse scheme (SFG 2D-IR) is designed to probe surfaces via sum-frequency generation between the 2D-IR signal and a non-resonant Vis or NIR pulse [3]. The latter is a fourth-order experiment, while the others are 5^{th} order experiments.

Here we present a novel 5^{th} order IR-UV/Vis-IR pulse scheme designed for the measurement of molecular exchange processes beyond the vibrational lifetime. Moreover, subensemble-specific photochemistry can be performed within a mixture of molecular species. The scheme is called VIPER 2D-IR (Vibrationally Promoted Electronic Resonance). An important feature of the new scheme, in contrast to triggered exchange spectroscopy which also uses an IR-UV/Vis-IR scheme, is that the pulse for electronic excitation is off-resonant. The resulting implications are explained below. Although the SFG method also includes a non-resonant Vis or NIR pulse, the interaction process is a different one, because in VIPER the UV/Vis pulse is used to transfer populations to the excited state, while in SFG it is used to up-convert to generated signal.

2. VIPER 2D-IR

In the visible spectral region it is often difficult to distinguish between multiple molecular species due to spectral overlap. IR spectroscopy is usually much more selective. However, the measurement of exchange between different species by 2D-IR EXSY spectroscopy is limited by the vibrational lifetime, which is typically a few picoseconds. In contrast, visible pump-probe spectroscopy probes excited states which exhibit lifetimes that can be several orders of magnitude longer than those in infrared spectroscopy. We use the ‘selectivity power’ of infrared spectroscopy and the long lifetime of electronically excited states to monitor chemical exchange processes in the infrared that occur on time scales that are much longer than the vibrational lifetime of the investigated species [4].

To achieve this goal, the VIPER 2D-IR pulse sequence (Figure 1A) makes use of an IR pulse that vibrationally tags a molecule, followed by an off-resonant visible pulse and an IR probe pulse. Only molecules that are vibrationally excited will be transferred to the electronically excited state, because the IR pulse shifts the molecule into resonance with the UV-Vis pulse. In this way a long lived 2D-IR signal is generated that allows to monitor chemical exchange until the initial ground state is repopulated. The population in the electronically excited state can perform exchange as well or undergo photochemistry. A strong vibronic coupling between the initially excited vibration and the electronic transition is not essential for the generation of a VIPER signal, because a modulation of the visible cross-section by intramolecular vibrational energy redistribution (IVR) into Frank-Condon-active modes may serve the same purpose [5]. This expands the applicability of the VIPER pulse sequence.

The VIPER pulse sequence has several important potential applications, which include the possibility to probe chemical exchange processes which occur on time scales that are slower than the vibrational lifetime (T_1), or to monitor the photochemistry of one particular molecular species within a mixture of species, even when they are in fast equilibrium. It is even feasible to probe exchange of molecules that are modified or destroyed by the visible

laser pulse, because they would produce a very long-lived or even a permanent ground state bleach. In this contribution we demonstrate the applicability of this scheme to monitor chemical exchange of two molecular species (hydrogen bonded vs free) on a time scale that is much longer than the vibrational lifetime, and show that it is possible to select one of these species within the mixture for electronic excitation.

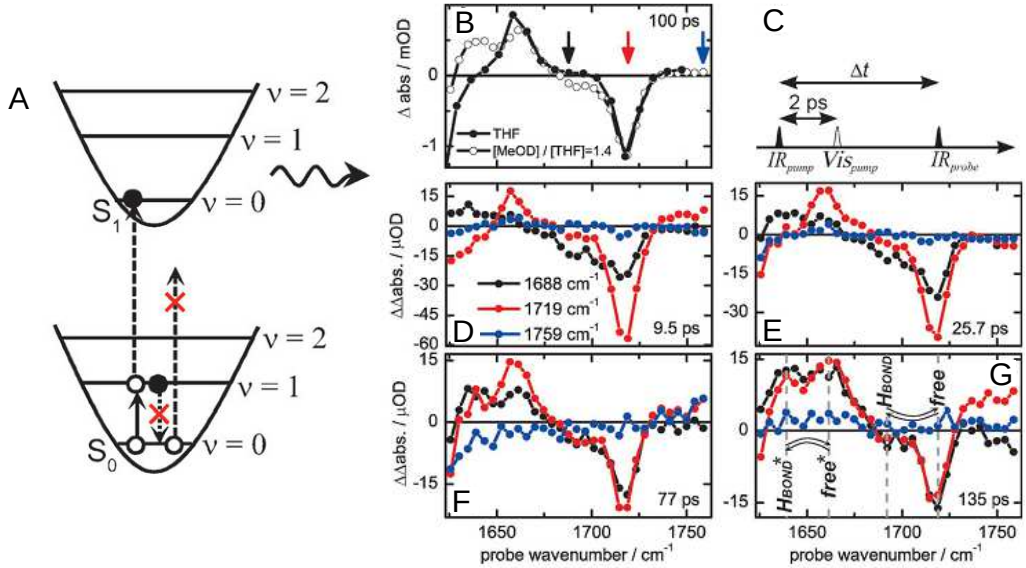

Figure 1. Principle of VIPER 2D-IR and its application [4]. A) In VIPER 2D-IR, the off-resonant Vis_{pump} (long-dashed arrow) is applied after the IR_{pump} (black arrow) and removes population from ν=1 (not from ν=0, long-dashed arrow with red cross), thereby preventing ground-state recovery (short-dashed arrow with red cross) and generating a persistent 2D-IR signal. The population on S_1 can relax with T_{el} or exhibit photochemistry (curved arrow). VIPER 2D-IR EXSY beyond T_1. B) TRIR spectra for C6 with and without MeOD in the C=O region. D–G) Cross-sections of the VIPER 2D-IR spectra of the sample with MeOD, pumped at the wavenumbers corresponding to the colored arrows in panel B. Note that signals at wavenumbers other than the IR pump correspond to cross-peaks. The delay time Δt (C) is depicted in (D)–(G), which share the same tick increment of 15mOD.

3. Chemical Exchange Beyond the Vibrational Lifetime

Our model system is the laser dye coumarin 6 (C6) which, upon addition of methanol, forms a dynamic equilibrium of methanol-associated and free coumarin molecules in solution [4]. The two species have distinct transient IR absorption bands (TRIR; see Figure 1B) which are assigned to the free and associated carbonyl of the C6, i.e. the band demonstrates a down-shift upon hydrogen bonding to methanol (for clarity all species have been labeled in Figure 1G). By using the VIPER pulse sequence (Figure 1C), we see that at 9.5 ps delay the VIPER spectra are very different (compare the black and the red spectra), best seen in the regions where the excited states of the associated and free species absorb (at 1639 cm^{-1} and 1657 cm^{-1}, respectively). This means that we observe transient IR spectra of a distinct species within a mixture of species, by selecting it via the IR pulse. In the normal TRIR spectrum (Figure 1B) both species are excited. In contrast, regardless of the species we excite with the IR pump pulse (denoted by the different colored arrows in Figure 1B), the 'end' spectrum we obtain at 135 ps is identical (and still being different at 77 ps delay). This means that chemical exchange has occurred on a time scale that is much slower than the vibrational lifetime of 1-2 picoseconds. Thus, we are able to follow a chemical exchange process with 2D-IR spectroscopy on a time scale that is far beyond the vibrational lifetime.

4. References

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